

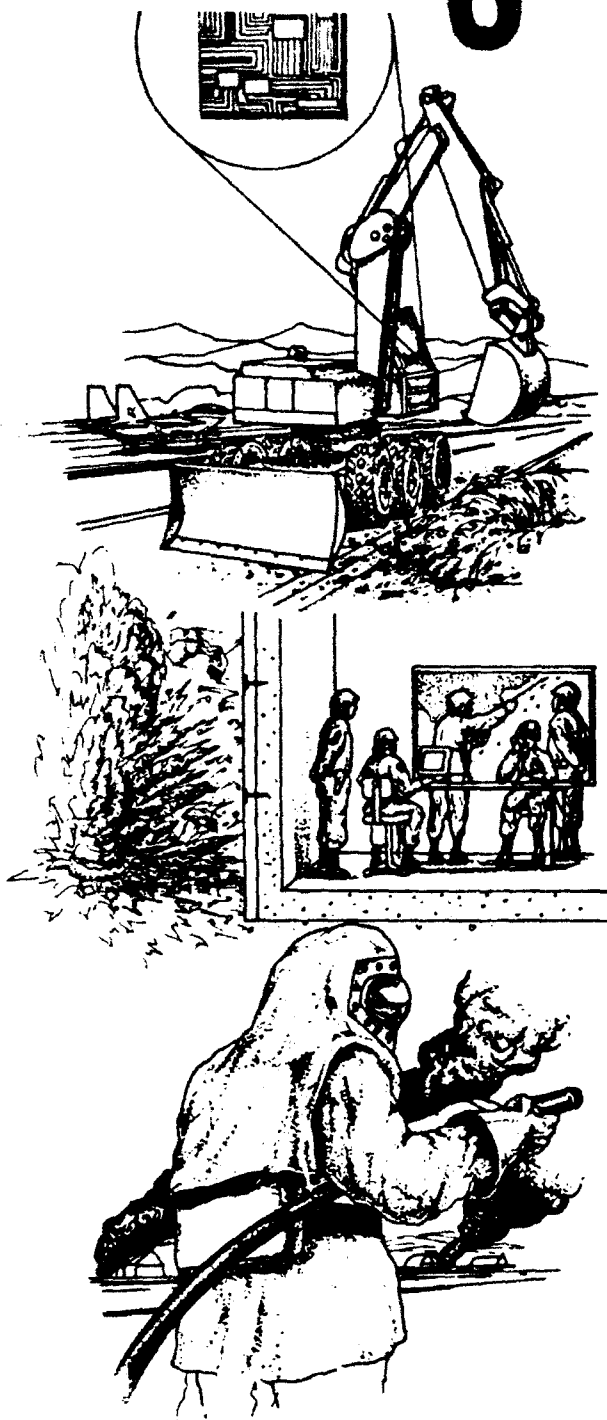
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## INDUSTRIAL WATER TREATMENT PRIMER

**SMSGT CLIFFORD SNIPE**

**HQ AFCESA/ENM  
TYNDALL AFB FL 32403-6001**

**MARCH 1992**

**FINAL REPORT**

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**AIR FORCE CIVIL ENGINEERING  
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## PREFACE

This report was prepared by HEADQUARTERS AIR FORCE CIVIL ENGINEERING SUPPORT AGENCY, SYSTEMS ENGINEERING (HQ AFCEA/EN), Tyndall Air Force Base, Florida 32403-6001. SMSgt Clifford Snipe, Mechanical Systems Superintendent, and Mr Freddie L. Beason, P.E., Mechanical Engineer, were the program technical managers. This report summarizes work accomplished between 11 February 1991 and 30 March 1992.

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This report has been reviewed by the Public Affairs Office and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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## SECTION I

### INTRODUCTION

This document provides a basic knowledge of industrial water treatment. The information in this document is written so that the average technician can understand and apply the concept of industrial water treatment.

#### A. OBJECTIVE

The objective of this document is to provide an information/instructional booklet for base-level technicians to develop and maintain an industrial water treatment program. The purpose of the program is to protect the heating and cooling infrastructure against scale and corrosion for maximum life expectancy, increase efficiency, and increase capacity.

#### B. BACKGROUND

##### 1. What is Water

The origin of all water supply is moisture that has evaporated from land masses and oceans and subsequently precipitated from the atmosphere (See Figure 1). It may descend from the clouds in the form of rain, snow, sleet, or hail to form rivers, lakes, ponds, and streams. Pure water is colorless, odorless, and tasteless. The chemical formula  $H_2O$  signifies that it is made up of two parts hydrogen and one part oxygen. To some degree, water can dissolve every substance on the earth and in the atmosphere. Because of this, water will contain impurities, which are the source of potential trouble in industrial water systems.

##### 2. Water Sources

a. The two principal sources of water supplies are groundwater (well) and surface water (lakes and rivers). Groundwater comes from sources such as wells, springs, and underground streams. Surface water comes primarily from rivers, lakes, and streams.

b. Groundwater is usually free of suspended matter but contains high concentrations of dissolved minerals. As rain and run-off water pass through the soil, suspended particles are filtered out and minerals in the ground dissolve into the water. Groundwater is relatively free of dissolved oxygen ( $O_2$ ) and high in carbon dioxide ( $CO_2$ ). The high content of  $CO_2$  in groundwater is the result of decay of organic matter in the surface soil.



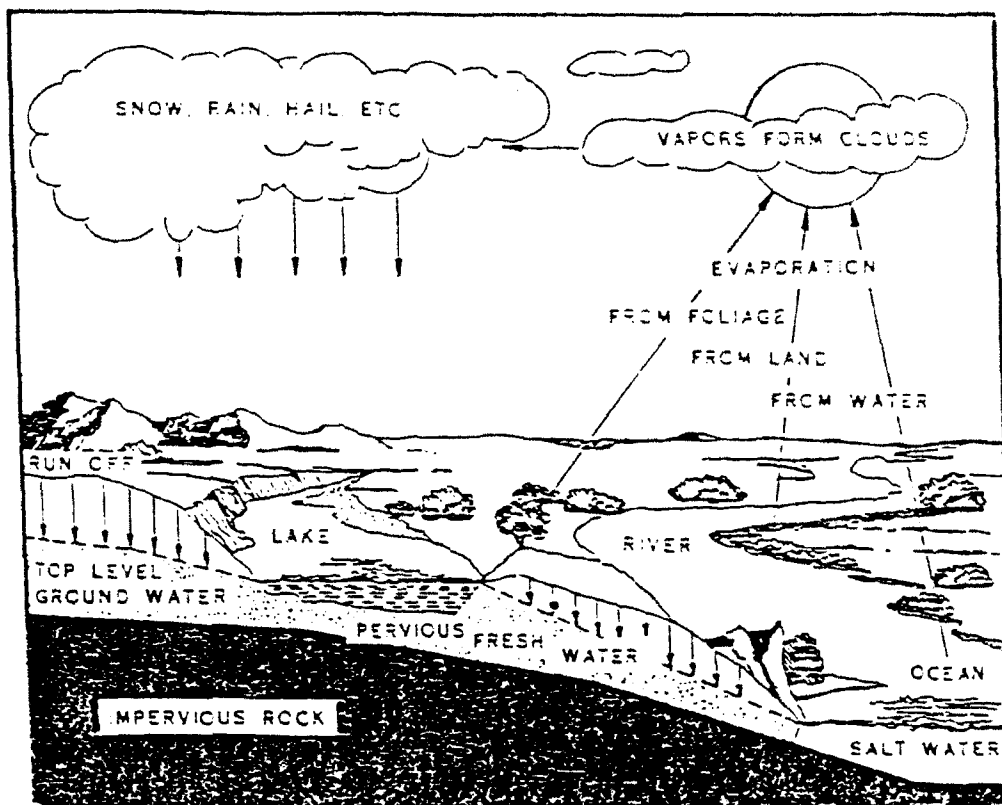


Figure 1. Hydrologic Cycle

c. Surface water, on the other hand, is known to be higher in suspended matter than groundwater. The dissolved oxygen content in surface water is high due to turbulence and its contact to the air. Surface water is the collection of rain and runoff that forms lakes, streams, and rivers. As the water flows across the land surface, minerals are dissolved. The force of the flowing water will also carry along fine particles and organic matter in suspension. Geographical location usually determine the types and quantities of dissolved minerals in the water supply.

### 3. Impurities Found in Water

#### a. Suspended Solids

(1) Turbidity is finely divided suspended particles that give the water an unsightly appearance. It can be caused by clay, silt, organic matter (dead plants and animals), inorganic matter, or microscopic organisms. It can cause sludge to form inside an industrial system which can lead to reduction of heat transfer and water flow restriction. Turbidity can also interfere with the proper operation of water treatment equipment. You can remove turbidity from water by sedimentation, coagulation, or filtration.

(2) Another form of suspended solids found in some systems are Microbiological organisms. They are divided into three separate categories:

(a) Deposit Producing Organisms - Slime forming microbes that deposit in heat exchangers and cause fouling.

(b) Corrosion Causing Organisms - Microbes that produce corrosive waste products that readily attack metals in cooling systems.

(c) Decay Causing Organisms - Organisms that convert the cellulose in wood structures to food and feed on the lignin/tannis, thus, causing the structure to weaken (also known as delignification). Cooling water systems are mostly affected by the problems associated with the presence of microbiological organisms.

#### b. Dissolved Gases

(1) Most dissolved gases show up in the form of oxygen and carbon dioxide. These gases are absorbed in water as the rain falls, the stream flows, and the water seeps through the earth's surface. Water also absorbs gases when it flows over decayed plants and animals.

(2) The extent of damages in a closed water system depends on the amount of makeup water added to the system. With the addition of makeup water come dissolved gases that continue the corrosion process on unprotected metal.

(3) Dissolved gases in the makeup water for steam heating systems is more damaging than for chilled and hot water systems. When makeup water enters a steam boiler, the gases vaporize and travel with the steam. As the steam condenses, oxygen escapes and attacks the upper surface of the condensate lines. Carbon dioxide combines with condensed steam to form carbonic acid which lowers the pH and corrodes the bottom section of the pipe.

(4) The majority of dissolved gases can be removed by mechanical means (deaeration and aeration). Chemicals are added to a system for complete removal or to mitigate the effects of the gases.

#### c. Dissolved Minerals

(1) Dissolved minerals are in water as a result of the water contact with other substances (i.e., soil, rocks). The amount of minerals dissolved in the water depends on the length of time the water is in contact with the minerals. These minerals show up in the form of deposits on the surface of the industrial system when the water is not treated. As stated earlier, groundwater is more apt to have high mineral content than surface water, so this discussion will focus primarily on the effects of untreated groundwater. Minerals such as calcium, magnesium, and silica are of major concern when considering makeup water for an industrial system. These minerals become more insoluble as the temperature of the water increases, thus leading to deposition in the system.

(2) Minerals combined with other ions:

(a) Calcium - When combined with bicarbonate, forms calcium bicarbonate. When heat is applied, carbon dioxide is released and calcium carbonate precipitates to form scale. When combined with sulfate, calcium sulfate is formed to produce a hard scale.

(b) Magnesium - When combined with bicarbonate, forms magnesium bicarbonate. When heat is applied, carbon dioxide is released and magnesium carbonate precipitates to form scale.

(c) Silica - Scale depositing

(d) Iron - Contributes to resin fouling

4. Purpose for Water Treatment

a. Water treatment programs are designed to protect the equipment in the system. The metallurgy of a system is critical when planning or designing a water treatment program, making sure that the end result is adequate protection of the metals.

b. A good water treatment program will help conserve energy by minimizing energy used to raise or lower water temperature. It will also reduce water consumption and lessen the chemical usage.

c. Equipment reliability also depends on the quality of the industrial water treatment program. Corrosion and scale buildup can cause premature equipment failure during peak operation. Scale deposition on a boiler tube can lead to tube rupture and ultimately boiler explosion.

d. Reduced labor cost is another end product of an effective water treatment program. It takes less man-hours and manhours to perform scheduled maintenance on systems that are free of scale deposits, microbiological growth, and corrosion by-products.

C. SCOPE

This document covers the basic elements of industrial water treatment for heating and cooling systems. It explains the impurities found in water sources and what can be expected if untreated water is used in an industrial system. It contains information on how to initiate and maintain a water treatment program. Treatment chemicals are explained and methods to monitor, feed, and evaluate their effectiveness are also discussed.

## SECTION II

### STEAM SYSTEM SURVEY

#### A. GENERAL

An important consideration for the water analyst is to assure that the boiler water will not contaminate the potable water system if the main supply line breaks. A backflow prevention device is designed to prevent such occurrence. This device should be installed on the raw water makeup to all boilers. For chemical mixing tanks, an air gap (space between the water level and faucet) can be used to provide the same protection.

Sampling points should be installed and identified in a steam system. The water analyst should be able to get a water sample from the boiler, the condensate return, and the deaerator without being exposed to the danger of severe scalding. To eliminate this hazard, a sample cooler (cooling coil) should be installed at each of these locations (See Figure 2). The sample cooler is simply a device installed to lower the water temperature at the selected sampling points. It allows cold water, usually potable water, to flow across a coil containing the system's water. The desired sample temperature is 70°F - 100°F.

Lowering the sample temperature also eliminates the possibility of the sample flashing to steam. Flashing occurs when water from a heated pressurized vessel is exposed to the atmosphere. If the sample flashes to steam, a small percent of the water vaporizes and causes an increase in dissolved solids; therefore, the sample is no longer representative of the water in the system and the results can be misleading.

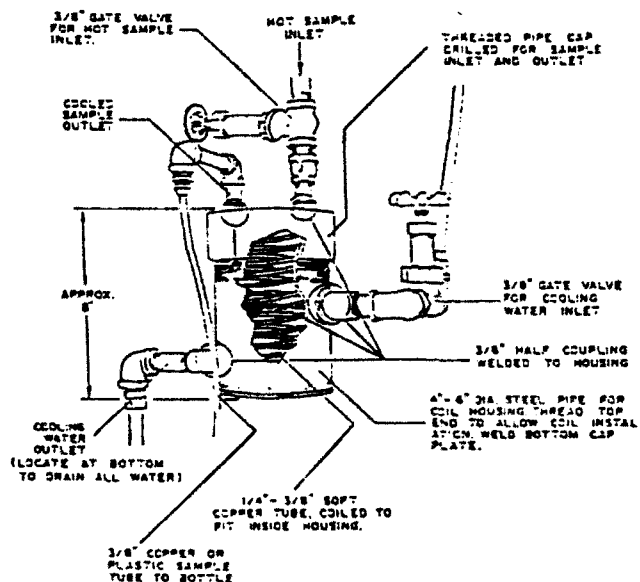


Figure 2. A Sample Cooler

Feeding chemicals into the system can be done using several methods or a combination of methods. Continuous feed pumps are the best and most reliable method for high pressure steam systems. Continuous feed pumps offer a smooth, even flow of chemicals without high or low swings of residual. To get the best performance and reliability, the feed pumps must be properly set-up and adjusted as the need varies. A typical system uses a pump to feed treatment chemicals into the steam drum or in the boiler feedwater line. Another feed pump injects amine into the steam header using stainless steel quills, and a third pump injects an oxygen scavenger into the deaerator (See Figure 3).

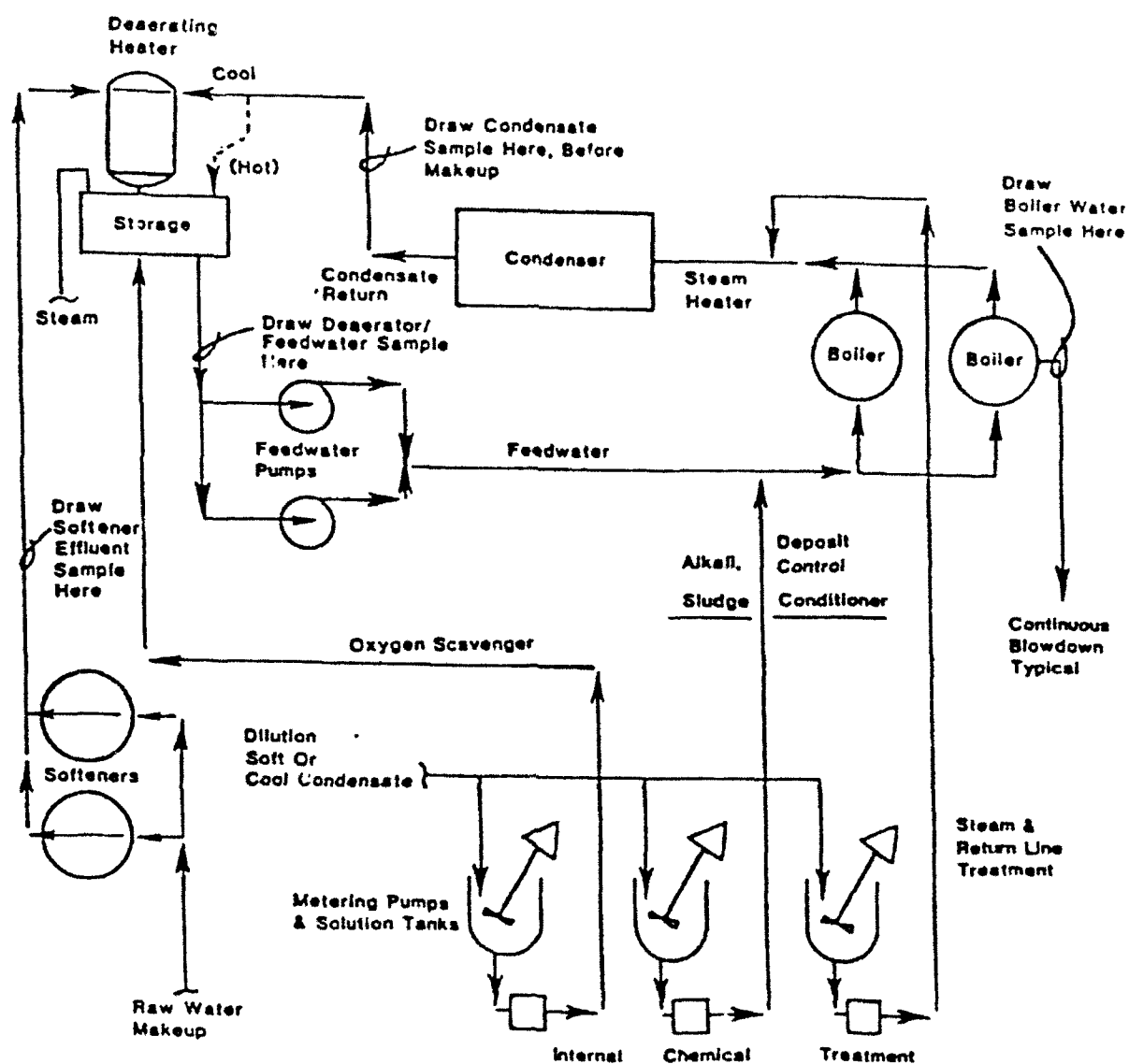


Figure 3. Chemical Feed And Sampling Points

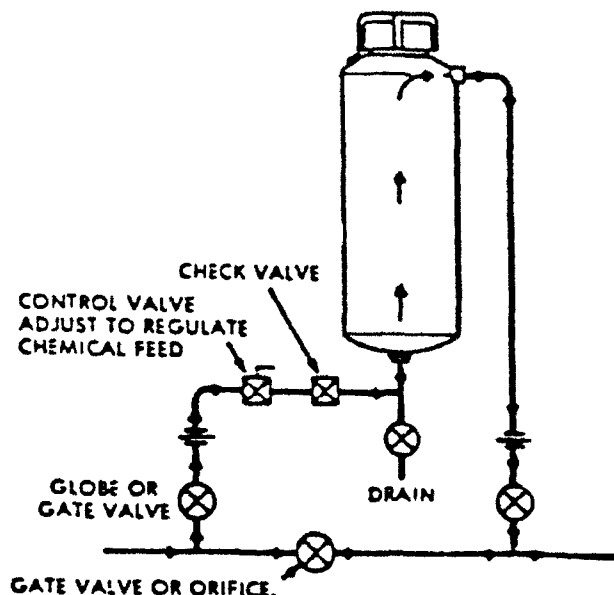


Figure 4. Bypass Pot Feeder

Low pressure steam systems are usually equipped with pot feeders (slug/shot feeder) to inject chemicals into the systems (See Figure 4). This type of chemical feeder is installed in a bypass loop of the boiler feedwater line. When the chemical residual in the boiler is low, the treatment chemical(s) is put in the pot feeder, the feedwater is then routed through the bypass loop, and this action forces the chemicals into the boiler. On some low pressure steam systems, chemical feed pumps are used to inject the amine into the steam lines. The most undesirable method of feeding chemicals into a system is by putting the chemicals in the condensate tank or the feedwater tank. This method does not always provide for proper mixing and the chemicals can cause the tank to corrode.

#### B. IMPURITIES FOUND IN A STEAM SYSTEM

The concentration of impurities in water is measured and expressed as parts per million (ppm). Parts per million is a measure of proportion by weight such as one pound in a million pounds.

A majority of the scale forming impurities and dissolved gases can be removed from boiler feedwater with pretreatment. In the event pretreatment is not available, chemical treatment is required to control these impurities that may be in the boiler water.

Oxygen and carbon dioxide can be detrimental to a steam system. These gases are most destructive in the condensate lines causing localized pitting and channeling of the pipes. Calcium, magnesium, and silica are minerals that can precipitate out of the water to form scale on the heating surfaces. Dissolved iron can precipitate and form sludge deposits in the boiler.

### C. TEST METHODS (See APPENDIX B)

Dissolved oxygen content in the water can be measured with a dissolved oxygen meter or chemical titration method. Carbon dioxide can be measured with a color comparator test kit.

The pH can be determined with litmus paper, pH colorimetric method, or a pH meter. The litmus paper and the color metric method are good to determine the approximate pH range. A calibrated pH meter is the most reliable way to measure acidity and alkalinity of the water.

The conductivity meter is used to determine the specific conductance and is expressed as micromhos (umhos), which is the ability of water to conduct electricity. The conductivity is based on the amount of dissolved solids in the water. An increase in dissolved solids means an increase in conductivity; therefore, the total dissolved solids can be determined by a calculation of the conductivity. A rule of thumb for calculating the total dissolved solids is to multiply the conductivity reading by 0.66 ( $0.66 \times \text{umhos} = \text{TDS}$ ).

Calcium, magnesium, and silica are leading contributors of scale depositing minerals. Sulfate, chlorides, and alkalinity (carbonates and bicarbonates) are dissolved ions that combine with other minerals to cause problems in a system.

Once the water has been analyzed and the amount of impurities is known, the analyst can determine the necessary steps in treating the boiler feedwater.

### D. BOILER WATER PRETREATMENT

#### 1. Dissolved Gas Removal

a. Aeration is a process used to remove carbon dioxide from the boiler feedwater (See Figure 5). The water is distributed at the top of the tank and free-falls to a collection basin at the bottom. The forced-draft degasifier blows an air stream countercurrent to the water flow. The undesirable gas escapes through the vent on the top of the aerator. A disadvantage to this process is that the water is saturated with oxygen after aeration.

b. Deaeration is a mechanical process used to remove noncondensable gases (oxygen and carbon dioxide) in the boiler feedwater (See Figure 6). The deaeration process involves heating the makeup water and the condensate return in a pressurized vessel to drive off the noncondensable gases. Trays or spray heads are used to break the water into small droplets. Steam is used to heat these droplets to the boiling point. As the water temperature increases, the gases are liberated and released to the atmosphere through the deaerator vent. Deaeration is especially necessary if there is an aerator in the system that saturates the water with oxygen.

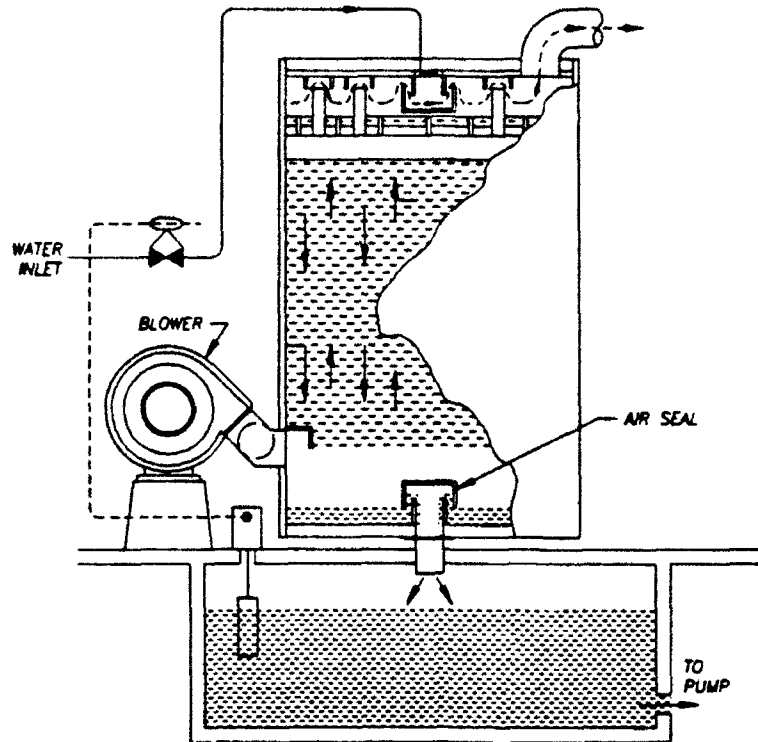


Figure 5. Forced Draft Degasifier Blows Air Through the Packing Countercurrent to the Downward Flow of Water to Remove  $\text{CO}_2$ .

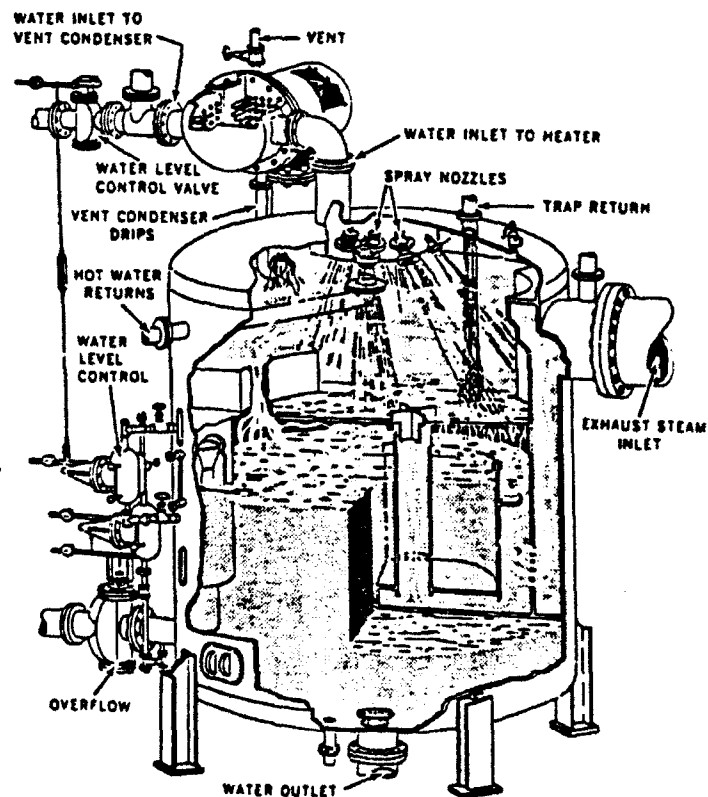


Figure 6. Spray Type Deaerator



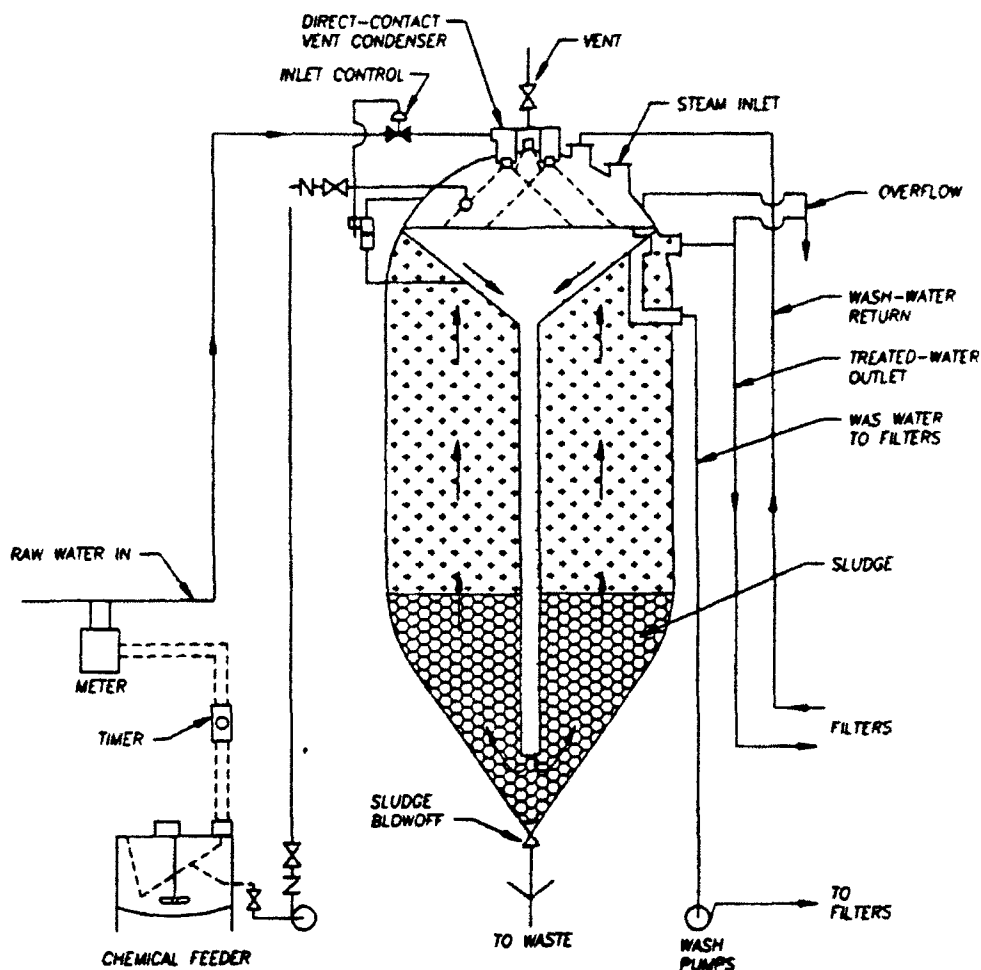


Figure 7. Hot Lime Softener. Steam mixes with raw water and chemical in the upper zone. Water flows to the bottom, rises through the sludge blanket, and discharges to the anthracite filters.

## 2. Dissolved Minerals Removal

### a. Precipitation Softening (Lime Soda)

(1) Hot lime softening (Figure 7) is accomplished in a pressure vessel at temperatures between 220°F to 240°F. The source of heat is live or exhaust steam. Hydrated lime is added to the water and reacts with calcium and magnesium to form calcium carbonate sludge. The insolubility of magnesium hydroxide increases at this high temperature resulting in a greater reduction of hardness minerals. Hot lime units operating at high temperatures will drive off any CO<sub>2</sub> and O<sub>2</sub>, thus reducing the additional chemical needed to control CO<sub>2</sub> and O<sub>2</sub>. This process uses anthracite (coal) filters to remove any floc that carryover with the processed water.

(2) Cold lime softening involves precipitation of the hardness impurities and discharge it in the form of a sludge. Hydrated lime is added to the water and reacts with calcium and magnesium to form calcium carbonate sludge. The scale depositing minerals are not completely removed with the hydrated lime alone. Additional reduction of these minerals is attained by supplementing the lime with soda ash and sodium aluminate. Silica reduction is also attained because it precipitates with magnesium hydroxide.

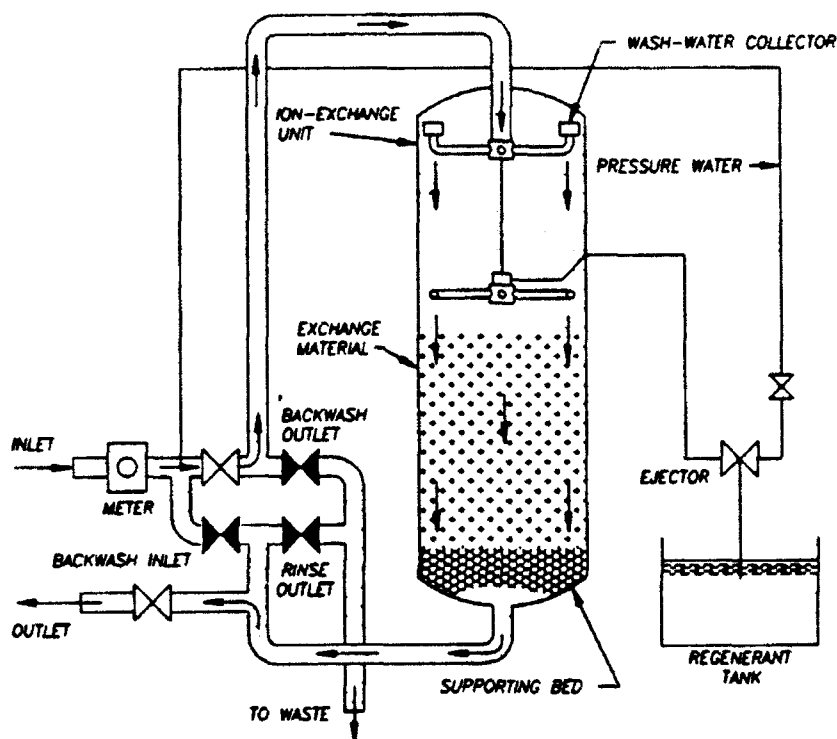


Figure 8. Typical Ion Exchange Unit Showing Service Flow Valve Nest for Resin Regeneration (Backwashing, Injection of Regenerant, and Rinsing).

#### b. Ion Exchanger

(1) Sodium zeolite softening was one of the first industrial applications of ion exchange. The primary purpose of sodium zeolite softening is to remove the scale forming ions of calcium and magnesium. This ion exchanger consists of an exchange medium (zeolite resins) that has the ability to exchange sodium ions for hardness ions (calcium and magnesium) upon contact (See Figure 8). In operation, the water passes through a layer of zeolite material which releases the sodium ions and retains the hardness ions. Over a period of time the resins become saturated with hardness ions and the exchange process comes to a halt. When this occurs the softener needs to be regenerated. To regenerate the softener, a strong

concentration of sodium solution is used to wash away the hardness ions, and restore the sodium ions on the zeolite resins. One disadvantage of sodium zeolite softening is that hardness is removed without alkalinity reduction. However, the advantages are a safe regenerate (salt), cost savings, and nonhazardous discharges.

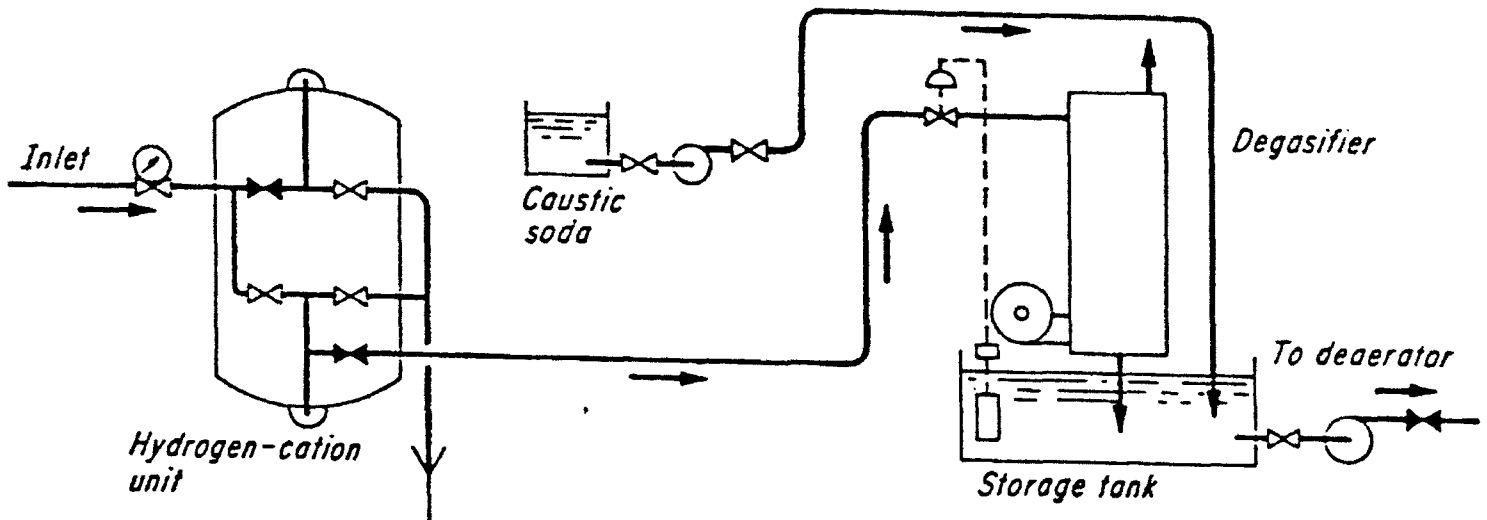


Figure 9. Hydrogen-Cation Unit Destroys Bicarbonate and Carbonate Alkalinity. Degasifier reduces  $\text{CO}_2$ . Caustic soda raises pH to desired level. (Courtesy of Power: McGraw-Hill Publications)

(2) A hydrogen zeolite softener (Figure 9) uses acid instead of salt to regenerate the resins. The hydrogen ions are exchanged for calcium, magnesium, and sodium ions. This type of softening is often used for water that is high in hardness and high in bicarbonate alkalinity. The following disadvantages are associated with the hydrogen zeolite softener:

(a) The acid used in the regeneration process makes the effluent water more corrosive (lower pH on effluent).

(b) The hazards that exist in handling the acid.

(c) The additional expense incurred for initial installation, chemicals, and corrosion resistant materials.

An aerator is often installed to dispel the carbon dioxide picked up in the softening process.

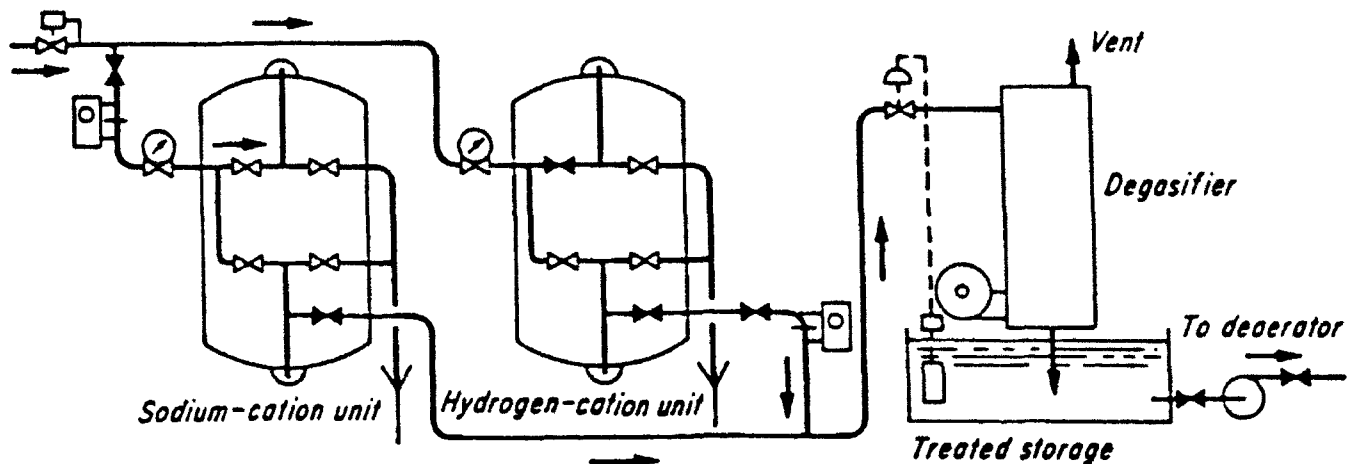


Figure 10. Split-Stream Dealkalizer Blends Water From Hydrogen and Sodium Units. Degasifier reduces  $\text{CO}_2$  (Courtesy of Power: McGraw-Hill Publications)

(3) A split-stream dealkalizer (See Figure 10) is used in areas where the water must be softened and dealkalized before it can be put to use in an industrial system. Sodium zeolite/hydrogen zeolite split-stream softening divides the flow of water through a parallel arrangement of a sodium zeolite exchanger and a hydrogen zeolite exchanger. Water passes through the two units and the effluents are blended to produce water of a desired alkalinity. Decarbonation for  $\text{CO}_2$  removal is necessary for the blended product. Regeneration is accomplished for these units in the same manner as previously stated.

#### E. INTERNAL WATER TREATMENT

Although the boiler feedwater has completed the process of pretreatment, it may still require additional treatment once it enters the boiler. Internal treatment is an essential element to the overall industrial water treatment program. Internal treatment complements external treatment by removing any impurities in the boiler that escape during pretreatment. Internal treatment is accomplished by using a variety of chemicals that will either eliminate the problem causing impurities or condition the impurities to prevent damage to the system.

##### 1. Boiler Water Treatment Guidelines

a. The two main considerations for treatment are the boiler operating pressure and the amount of hardness in the boiler feedwater.

b. Better control of treatment program is required as the pressure in the boiler increases. Since the boiler is much more critical at high pressures, less hardness and dissolved solids can be tolerated.

c. Boiler water treatment is to prevent scale, corrosion, and carryover (priming and foaming). The scale is primarily due to the presence of calcium and magnesium hardness in the water. Silica is also a contributing factor. Corrosion is due to the presence of carbon dioxide and oxygen; and carryover is the result of high water level and high solids in the boiler water, or sudden load swings.

d. External treatment is usually the first line of defense against scale deposits in the boiler. If external treatment is not available, scale can be controlled within the boiler with internal treatment. Controlling silica in the boiler is only accomplished with blowdown. The higher the operating pressure, the greater the need of external treatment.

e. Low pressure boiler corrosion due to oxygen is primarily controlled with oxygen scavengers. High pressure systems may require external oxygen removal equipment (deaerating heaters) which should remove the majority of oxygen. An oxygen scavenger is also used to eliminate any remaining oxygen that enters the boiler.

f. Antifoam chemicals are used to control foaming and carryover in steam boilers.

g. The types of scale control treatment within the boiler can be described as sludge conditioning and solubilizing type of treatment. Sludge conditioning allows the hardness to precipitate, the sludge is then treated to prevent baking-on to the heat transfer surface (See Figure 11). The solubilizing type of treatment maintains the hardness in a soluble condition. Sludge conditioning becomes more favorable when the hardness in the makeup water is high.

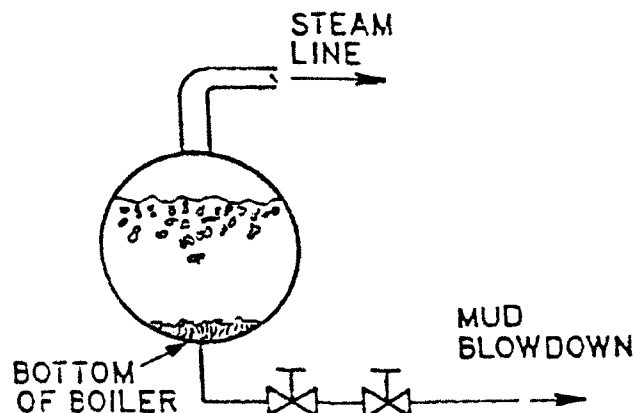


Figure 11. Precipitated Minerals. Sludge is formed at the bottom of the boiler as minerals precipitate.

## 2. Chemicals

a. Orthophosphate - Prevents calcium carbonate and calcium sulfate scales. Combines with calcium to form calcium phosphate which breaks down to form a fluid like sludge.

b. Sodium Lignosulfonate - Ensures sludge is in a fluid state with the proper characteristic for removal by blowdown.

c. Sodium Hydroxide - Prevents magnesium phosphate scale formation and corrosion. Controls the alkalinity and maintains the desired pH (usually 10.5 to 11.5).

d. Sodium Sulfite - Prevents oxygen corrosion on the steam side; oxygen scavenger.

e. Morpholine - Neutralizes the acid condition to prevent carbonic acid corrosion in the condensate return system. Short run.

f. Cyclohexylamine - Neutralizes the acid condition to prevent carbonic acid corrosion in the condensate return system. Long run.

g. Octadecylamine - A protective barrier is deposited on the pipe surface to prevent corrosion in the condensate return system. Filming amine.

## 3. Blowdown

a. Sometimes it may be necessary to remove a portion of the boiler water by blowdown to control the concentration of total solids. The objective is to maintain a balance between treatment and blowdown so that the treatment chemical residuals remain within the prescribed ranges and the solids are kept within a safe operating limit.

b. Small low pressure boilers are equipped with a manual bottom blowdown, while larger high pressure boilers may have a continuous blowdown line located in the steam drum and a bottom blowdown on the mud drum. In either case, it is best to use short duration blowdown and give the boiler time to fully recover before any subsequent blowdown. Refer to Table 1 for boiler operating ranges and limits.

## 4. Oxygen Removal Process

a. A major contributor to corrosion that occurs in any industrial water system is oxygen, dissolved or free. The most common method for removing dissolved oxygen in a high pressure system is mechanical deaeration. To assure complete oxygen removal, sodium sulfite is added to the feedwater to maintain a residual in the boiler water. In low pressure systems, sodium sulfite alone will suffice for scavenging oxygen.

TABLE 1. LIMITS ON BOILER WATER CONDITIONS  
FOR AN EFFECTIVE TREATMENT PROGRAM

Boiler Pressure (psig)	Maximum TDS (ppm)	Maximum Conductivity (umho)	Maximum Silica (ppm)	Range Sulfite (ppm SO <sub>3</sub> )	Range *Phosphate (ppm PO <sub>4</sub> )	Range *Alkalinity (ppm CaCO <sub>3</sub> )	Ligno- sulfonate (ppm)
0-15	6000	9000	200	30-60	30-60	300-500	70-100
16-149	4000	6000	200	30-60	30-60	220-500	70-100
150-299	4000	6000	150	30-60	30-60	220-500	70-100
300-449	3500	5250	90	20-40	30-60	180-450	70-100
450-599	3000	4500	40	20-40	30-60	170-425	60-90
600-749	2500	3750	30	15-30	30-60	170-425	50-80
750	2000	3000	20	15-30	30-60	170-425	40-70

\*Note: Ortho-Phosphate  
Hydroxyl Alkalinity (Causticity)  
Sodium Lignosulfonate (as tannic acid)  
Range

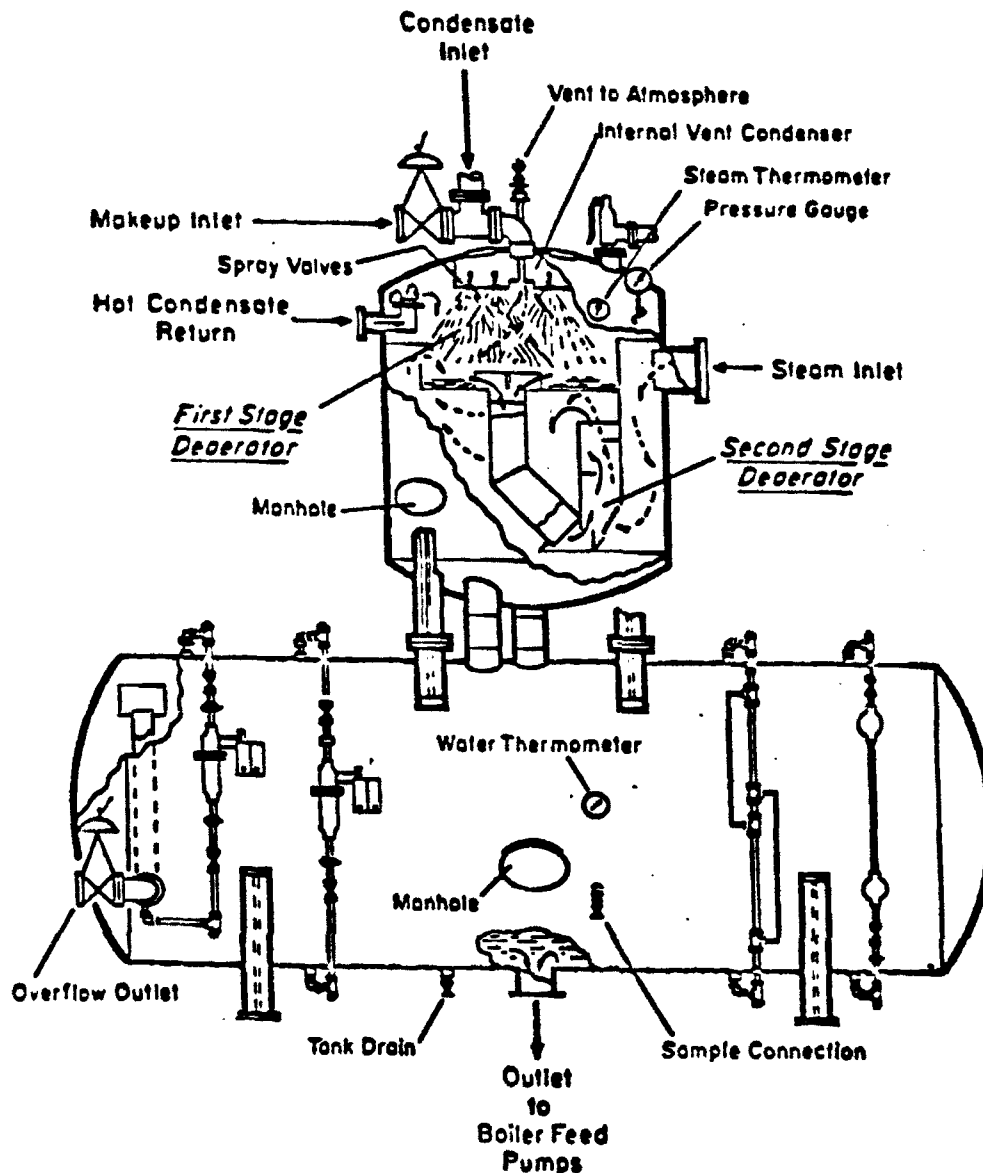


Figure 12. Spray Type Deaerator with Feedwater Storage Tank. (Courtesy of Puckorius & Associates)

b. Deaeration is a mechanical process used to remove dissolved oxygen and dissolved carbon dioxide in the boiler feedwater (See Figure 12). The deaeration process involves heating the makeup water and the condensate return in a pressurized vessel to drive off the noncondensable gases. Trays or spray heads (located in the deaerator) are used to break the water into small droplets. Refer to Table 2 for pressure/temperature corresponding chart. Steam is used to heat these droplets to the boiling point. As the water temperature increases, the gases are liberated and released to the atmosphere through the vent. Deaeration is especially necessary if pretreatment includes aeration.



TABLE 2. GUIDE FOR FEEDWATER HEATER OPERATION  
BOILING POINTS CORRESPONDING TO VARIOUS ELEVATION  
Degrees in Fahrenheit

Sea Pressure In Level Heater P.S.I.G.	ELEVATION												
	500	1000	1500	2000	2500	3000	3500	4000	4500	5000	5500	6000	
	TEMPERATURE												
.0	*212	211	210	209	208	207	207	206	205	204	203	202	*201
.5	214	213	*212	211	210	209	208	208	207	206	205	204	203
1.0	215	215	214	213	*212	211	210	209	208	208	207	206	205
1.5	217	216	215	215	214	213	*212	211	210	209	208	208	207
2.0	219	218	217	216	215	215	214	213	*212	211	210	209	208
2.5	*220	219	219	218	217	216	215	215	214	213	*212	211	210
3.0	222	221	*220	219	219	218	217	216	215	215	214	213	*212
3.5	*223	222	222	221	*220	219	219	218	217	216	215	215	214
4.0	224	224	*223	222	222	221	*220	219	219	218	217	216	215
4.5	226	225	224	224	*223	222	222	221	*220	219	219	218	217
5.0	227	227	226	225	224	224	*223	222	222	221	*220	219	219
5.5	229	228	227	227	226	225	224	224	*223	222	222	221	*220
6.0	231	230	229	228	227	226	225	224	223	222	221	220	219
6.5	232	231	230	229	228	227	226	225	224	223	222	221	220
7.0	233	232	231	230	229	228	227	226	225	224	223	222	221
7.5	234	233	232	231	230	229	228	227	226	225	224	223	222
8.0	235	234	233	232	231	230	229	228	227	226	225	224	223
8.5	236	235	234	233	232	231	230	229	228	227	226	225	224
9.0	237	236	235	234	233	232	231	230	229	228	227	226	225
9.5	238	237	236	235	234	233	232	231	230	229	228	227	226
10.0	240	239	238	237	236	235	234	233	232	231	230	229	228
10.5	241	240	239	238	237	236	235	234	233	232	231	230	229
11.0	243	242	241	240	239	238	237	236	235	234	233	232	231

Temperatures are shown to the nearest whole degree.  
Elevations are given in feet.  
\*Exact

c. Adjusting the deaerator vent valve to eliminate the maximum amount of condensible gases while venting the least amount of steam will optimize the deaerator operation. The optimum vent valve opening is established by following the procedures below:

- (1) Stop feeding sodium sulfite.
- (2) Wait for the boiler to use an equivalent of ten times the deaerator storage capacity.
- (3) Open the vent valve fully.
- (4) Measure the oxygen content in the feedwater.
- (5) Close vent valve one full turn and repeat dissolved  $O_2$  test.
- (6) Continue step 5 until the  $O_2$  content increases.
- (7) At this point open the vent valve 1/4 turn and measure  $O_2$  content.
- (8) Use the smallest vent opening which gives minimum  $O_2$  in the feedwater.
- (9) Resume sodium sulfite feed.

Once the final adjustment is made on the vent valve, a noticeable change in energy consumption can be expected.

d. Sodium sulfite is used to scavenge oxygen in most boilers. However, sodium sulfite can decompose at  $500^{\circ}\text{F}$  to produce an acidic gas; therefore, hydrazine is usually the oxygen scavenger of choice if the water temperature exceeds  $500^{\circ}\text{F}$ .

#### F. CONDENSATE LINE PROTECTION

When the boiler produces steam, the heat and pressure cause the alkalinity in the water to break down forming carbon dioxide ( $\text{CO}_2$ ) gas. The  $\text{CO}_2$  gas travels with the steam throughout the system. As the steam condenses,  $\text{CO}_2$  dissolves in the condensate to form carbonic acid. This acid condition lowers the condensate pH, which increases the corrosion rate of steel, and corrosion occurs on the water side of the condensate return pipe. This type of corrosion is commonly known as gouging or grooving (See Figure 13).

Oxygen also plays a role in corrosion of condensate return lines. Oxygen can get into the condensate system at valve glands, pump seals, infiltration of leaks, and at the condensate tanks.

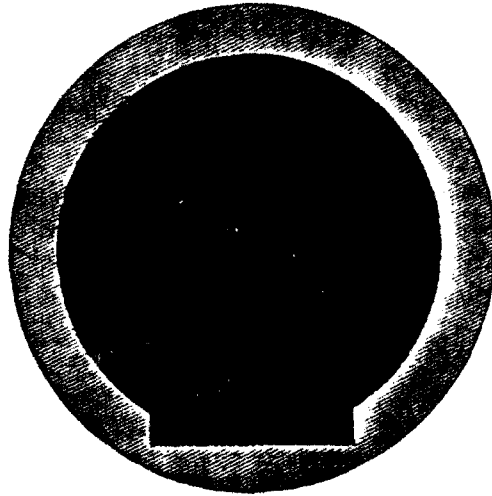


Figure 13. Channeling of Condensate Return Pipe due to Low pH of the Condensate.

If there is no deaeration or the deaerator is not operating effectively, dissolved oxygen enters the system in the feedwater. The presence of oxygen in the condensate system causes localized pitting inside the upper portion of the condensate return pipe.

An amine treatment program will protect condensate return systems from corrosion. Neutralizing amines are often used in steam systems to counteract the acidic condition created by the presence of carbon dioxide in the condensate. Filming amine forms a protective barrier on the inside of the condensate pipes to prevent oxygen pitting and carbonic acid corrosion.

Neutralizing amines such as morpholine and cyclohexylamine are used to stop gouging and grooving in the condensate system. As the temperature and pressure in the boiler increase, the amines vaporize and travel with the steam throughout the system. The high concentration of morpholine will be in the condensate at points closest to the plant (the point of initial condensation). Better protection can be expected at these points because morpholine is less volatile and readily condenses with the steam. Therefore, morpholine becomes less effective at distant points and will not provide adequate protection at the farthest points of the condensate lines for large systems. However, cyclohexylamine is more volatile and will travel a greater distance with the steam before it condenses, giving greater protection at the distant points in the system. A common practice for adequate condensate line protection in large systems is to provide a 50/50 mixture of morpholine and cyclohexylamine. Morpholine will provide good protection close to the plant and cyclohexylamine will protect the system at distant points. The percent of solution should be adjusted if adequate protection is not attained throughout the system (e g., low pH near the plant, adjust the mixture to 60% morpholine and 40% cyclohexylamine).

It is necessary to take condensate samples at different points throughout the system to ensure amine distribution. The method of determining adequate protection is by measuring the condensate pH, keeping the range between 8.0 and 8.5 at the test sites. Care should be taken not to overfeed neutralizing amines because pH above 8.5 can cause serious corrosion of any copper alloys in the system. If the pH cannot be maintained at the recommended ranges (low pH at distant point with the use of cyclohexylamine), it may be necessary to set up an additional injection point midway in the steam supply line.

When properly applied, a filming amine will prevent corrosion in the condensate pipes on the water side and the vapor side. The amine will replace loose oxide scales (corrosion products) with a nonwetting film on the interior surface of the condensate pipe from the point of condensation throughout the system. This film acts as a barrier between the metal and the condensate. The initial dosage will remove existing corrosion products which may cause severe maintenance problems unless the amine dosage is started at a very low rate and gradually increased over several weeks proportionate to the steam flow. The amine should be injected into the steam header with a stainless steel quill to ensure vaporization. Overfeeding filming amine will result in the formation of amine gunk and deposits in low flow areas which may plug screens, traps, and lines. Underfeeding will allow corrosion to occur at unprotected areas in the condensate system.

#### G. STEAM SYSTEM ANALYSIS

Water analysis of a steam system is done to determine the amount of treatment chemicals in the system so the dosage levels can be properly adjusted. Accurate test results depend on following good laboratory procedures and techniques. It is necessary to keep laboratory test instruments and test apparatus in good condition (calibrated and clean).

##### 1. Collecting Steam System Water Samples

- a. Open the cold water valve on the cooling coil until a steady stream is flowing through the sample cooler.
- b. Blowdown the sampling line to discharge the stagnant water.
- c. Throttle the sample line valve to allow a slow steady stream of the sample water. Ideally, the water temperature should be 70° to 100° F to prevent flashing and scalding.
- d. Rinse the sample bottle and cap at least two times with the system water.

e. Place the sampling tube near the bottom of the sample bottle and fill the sample bottle allowing the water to overflow the bottle.

f. Remove the sample tube, dispel any air bubble, and cap the bottle immediately.

g. Close the valve on the sampling line.

h. Close the valve on the cooling water line.

i. The sample should be analyzed within 2 hours after it is collected.

## 2. Performing Tests and Recording Data

a. Procedures for testing the water in the steam systems are outlined in Appendix B. A special test kit must be procured to measure the dissolved oxygen content.

b. The information gathered as a result of these tests is important data that should be used to evaluate the treatment program and make the necessary adjustments of the chemical application. It is important to record only the data that provides meaningful information for evaluation and adjustment.

## 3. Interpreting Test Data

It is important for the analyst to know the operating ranges of the recommended chemical residual and what it is supposed to accomplish in a system. Once the testing has been completed, the analyst needs to view the data, making note of anything out of the ordinary.

TABLE 3. TROUBLESHOOTING WATER SYSTEM

<u>Condition</u>	<u>Probable Cause</u>	<u>Action</u>
1. Hardness in boiler feedwater	a. Inoperative water softener.	Regenerate/repair water softener.
	b. Infiltration of raw water at convertors.	Take condensate samples at all steam convertors to pinpoint place of infiltration. Make necessary repair.
2. Dissolved oxygen in feedwater exceeds the recommended range.	a. Deaerator malfunction.	Check deaerator press/temp. Check deaerator vent valve to ensure the most effective opening.
	b. Feedwater pump sucking air at the seal.	Repair feedwater pump seal.
	c. Insufficient sodium sulfite residual.	Check sulfite feed system and make necessary adjustment/repair. Increase sodium sulfite feed rate.
3. Consistently low chemical residual in system (General)	a. Testing reagents shelf-life expired.	Replenish test reagents.
	b. Chemical feed pump inoperative or out of adjustment.	Repair or adjust chemical feed pump.
	c. Restriction in the chemical feedline.	Clean or replace chemical feedline.
	d. Mistake in chemical identification.	Make sure the chemical you are using is what you want.
	e. Inadequate amount of treatment chemical.	Increase chemical dosage.

TABLE 3. TROUBLESHOOTING WATER SYSTEM  
(Continued)

<u>Condition</u>	<u>Probable Cause</u>	<u>Action</u>
3. Consistently low chemical residual in system (cont.)	f. Makeup water increase due to leak in the system (boiler section or condensate).	Inspect boiler and condensate piping system for any indication of leaks. Make sure drain valves on condensate receiving tanks are closed.
		Check boiler blowdown valves to ensure 100% shut-off. Check continuous blowdown valves setting.
4. Low phosphate residual.	a. Increased hardness in feedwater.	Check water softener. See action for "Hardness in boiler feedwater."
	b. Wrong type/choice of phosphate.	Select phosphate based on the needed $PO_4$ percent to ensure the highest quality for the hardness content.
5. Low sulfite residual.	a. Chemical feed pump inoperative.	Check sulfite feed system and make necessary adjustment/repair.
	b. An increase of oxygen content in feedwater.	Check deaerator operation and make necessary adjustment/repair. Increase sodium sulfite feed rate.
	c. Improper sampling or testing technique.	Follow steps as outlined in "Collecting Water Samples." Test for sulfite first. Stir sample smoothly.

TABLE 3. TROUBLESHOOTING WATER SYSTEM  
(Concluded)

<u>Condition</u>	<u>Probable Cause</u>	<u>Action</u>
6. Total dissolved solids exceed the recommended range.	a. Insufficient boiler blowdown.	Increase blowdown rate. Adjust the surface blowdown valve.
	b. Excessive chemical addition.	Analyze boiler water to determine treatment chemical residual and make adjustments.
7. High total dissolved solids in condensate.	a. Boiler water carryover with the steam.	Reduce the total dissolved solids in the boiler by blowdown. Make sure water level is not too high.
	b. Too much amine injected.	Reduce amine injection, but maintain the recommended pH.
	c. Infiltration of raw water at convertors.	Take condensate samples at all steam convertors and test for hardness and TDS to find the point of infiltration. Make necessary repair.
	d. Active corrosion occurring in the system.	Analyze the condensate for iron /copper content. Ensure amine treatment is reaching all points in the condensate system.



## H. EVALUATING TREATMENT PROGRAM

The effectiveness of the water treatment program should be evaluated at least once a year during annual maintenance. At this time the operators can visually inspect the water sides of the boiler(s) for scale deposits, baked on sludge, and corrosion. The steam side can be inspected for pitting caused by oxygen attack. Nondestructive inspection devices such as eddy current, ultra sound, radiography, and fiber-optic are also available to provide a more comprehensive view of the interior of pipes, boiler tubes, and other related parts in the system. The condition of the boiler(s) should be documented for future reference and compiled for historical data.

Corrosion coupons are used in a steam system to monitor the effectiveness of the condensate treatment program. The coupon concept involves selecting a metal specimen that is the same metallurgy as found in the system. The coupon should be installed in the condensate return line so that it only contacts the condensate (See Figure 14). Typical test period range from a minimum of 30 days to a maximum of 90 days. The coupon is preweighed and has a known surface area. Upon completion of the test, it is cleaned and reweighed. The difference between the two weights represents the amount of metal lost. The rate of the metal penetration is traditionally reported as mils per year (mpy).

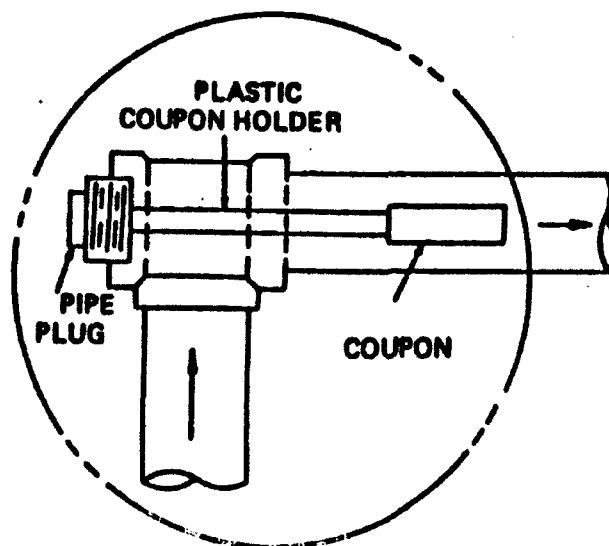


Figure 14. Installed Corrosion Coupon

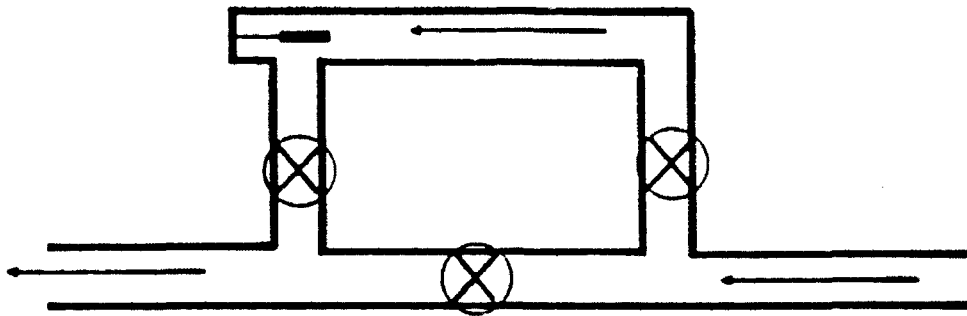


Figure 15. Condensate Bypass Arrangement

While the rate of corrosion never reaches zero, it can be small enough to be unmeasurable. A corrosion rack should be installed at distant points in the system, as well as points closest to the plant, to evaluate the effectiveness of the amines used. Use a bypass arrangement to facilitate the ease of installing and removing the coupons (See Figure 15).

Evaluation can be accomplished using one or more of the methods listed above.

#### I. PROPRIETARY TREATMENT PROGRAM

Some installations may choose to use proprietary chemicals in their systems. Chemical representatives that sell to government agencies usually provide service and technical assistance to the bases that use their products. Bases tend to rely solely on their service and technical assistance and give up on developing in-house expertise.

Suggested guidelines for using proprietary chemicals:

1. Make sure the treatment program is developed for your water and your mechanical system based on Air Force procedures.
2. Find out what each mixture is supposed to do. Secure a copy of the product fact sheet and the material safety data sheet.
3. Check to see that it is doing what it is supposed to do. This may include direct feedback from water analysis and corrosion coupons.
4. Take an active role in monitoring the program; don't assume the representative is doing it for you.
5. Take advantage of any training opportunity the chemical supplier makes available.

6. If anything goes wrong or doesn't seem right, demand an explanation from the chemical representative.

7. Set a realistic goal for developing and initiating an in-house program that will free you from depending on an outside source.

## SECTION III

### HOT WATER HEATING SYSTEMS

#### A. GENERAL

A water treatment program for a hot water heating system is less complicated and less demanding than the treatment program for a steam heating system. Unlike a steam system, a hot water system is a closed system and does not require blowdown; therefore, system makeup should not exceed 5% of the system's volume/year. The chemicals used in a hot water system are retained within the system, making it cost-effective and easier to maintain.

The following tasks should be accomplished before a water treatment program is initiated for a hot water heating system.

1. Make sure the system is free of leaks.
2. Install a backflow prevention device in the makeup water line.
3. Install a metering device.
4. Install a sample cooling coil.
5. Install a chemical feed system.
6. Install dielectric unions.

#### B. TYPES OF HOT WATER SYSTEMS

Low/medium temperature water systems do not require pretreatment of the makeup water unless the total hardness exceeds 50 ppm as  $\text{CaCO}_3$ .

Three treatment programs developed for closed systems are:

1. Sulfite-caustic soda program
2. Nitrite-borax program
3. Molybdate-caustic program

Nitrite-borax and molybdate-caustic treatment programs are usually the programs of choice for low/medium temperature systems because they are very effective at temperatures below  $250^{\circ}\text{F}$ . The treatment program is selected based on the metals in the heating system and the cost of the treatment program. Factors influencing the cost of a program include the size of the system, the amount of makeup water required, and the environmental or health restrictions.

High temperature water (HTW) systems operate at 350°F to 420°F. The major concern for this system is to prevent scale deposition in the boiler tubes. Water softeners should be installed to remove 100% of the hardness contributing minerals from the makeup water. Scale on boiler tubes in a HTW system can lead to tube rupture or a boiler explosion. The chemical treatment program most often used for a HTW system is the sulfite-caustic soda program.

### C. TREATMENT PROGRAMS

#### 1. Nitrite-Borax Treatment Program

a. For the initial dosage, add approximately 18 lbs of sodium nitrite-borax for every 1000 gallons of water in the system. Enough sodium nitrite-borax should be added to sustain a nitrite residual of 1000 ppm as nitrite ( $\text{NO}_2$ ).

b. Maintain a nitrite residual of 600 to 1000 ppm.

c. Add sodium carbonate to maintain the pH at 8.5 to 9.5.

d. Check pH and analyze the system water to determine the nitrite content 24 hours after initiating treatment.

e. Make necessary adjustments if needed.

#### 2. Molybdate-Caustic Soda Treatment Program

a. For the initial dosage, add approximately 12 lbs of sodium molybdate for every 1000 gallons of water in the system. Enough sodium molybdate should be added to sustain a molybdate residual of 125 ppm as  $\text{MoO}_4$ .

b. Maintain a Molybdate residual of 100 to 125 ppm.

c. Add sodium hydroxide to maintain the pH at 8.5 to 9.5.

d. Check pH and analyze the system water to determine the molybdate content 24 hours after initiating treatment.

e. Make necessary adjustments if needed.

#### 3. Sulfite-Caustic Soda Treatment Program

a. For the initial dosage, add approximately 1 lb of sodium sulfite and 2 lbs of sodium hydroxide for every 1000 gallons of water in the system.

- b. Maintain a sodium sulfite residual of 50 to 100 ppm as  $\text{SO}_3$ .
- c. Add sodium hydroxide to maintain the pH at 9.0 to 10.0.
- d. Check pH and analyze the system water to determine the sulfite content 24 hours after initiating treatment.
- e. Make necessary adjustments if needed.

## SECTION IV

### CORROSION CONTROL FOR CLOSED SYSTEMS

#### A. GENERAL

Water in a closed recirculating system is completely confined within the system. The most serious problems closed recirculating water systems encounter are corrosion and corrosion product fouling. Corrosion is an electrochemical process by which metals return to their native state. For example, mild steel reverts to iron oxide. When corrosion occurs, the corrosion products accumulate in the system and form deposits throughout the heat exchangers, piping, etc. The corrosion process contributes to the destruction of costly equipment, decreases the efficiency/capacity, and causes considerable downtime and costly production losses. Chemicals are introduced into the system to control the corrosion process.

Corrosion control in closed water systems requires the following:

1. Knowledge of the makeup water characteristic.
2. Knowledge of the metals used in the system.
3. Awareness of their susceptibility to the corrosion at the operating conditions found in the system.
4. Familiarity with the limitations of the chemicals used for corrosion control.

A number of characteristics can influence the amount and rate of corrosion that will occur. The most important ones are:

1. Oxygen content
2. Water velocity
3. Temperature
4. Microbial growths

#### B. TYPES OF CORROSION

The three basic types of corrosion attack that occur are:

1. General attack - a term that describes the uniform distribution of corrosion over an entire metal surface. The large amount of iron oxide produced through general attack contributes to the severe fouling problem.

2. Localized or Pitting Attack - Occurs when isolated metal areas are corroded. Pitting is the most serious type of corrosion because all the corrosive action is concentrated in a very small area. Pitting attack can cause metal to perforate in a very short time, causing pinhole leaks in the piping.

3. Galvanic Attack - Occurs when two different metals are in physical contact. In such a case, the more active metal corrodes rapidly. Common examples in a water system are steel and brass, aluminum and steel, zinc and steel, and zinc and brass. In each case, the first metal of the pair will corrode.

a. A simple example of galvanic corrosion between two dissimilar metals is a steel pipe screwed into a bronze valve or copper tubes joined to a mild steel tubesheet in a heat exchanger.

b. An example of galvanic corrosion in action is depicted in Figure 16. Positive ions flow through the electrolyte from the anode to the cathode. At the same time, electrons flow through the metallic path from the anode to the cathode.

### C. CORROSION INHIBITORS

One approach for preventing or minimizing corrosion in the system is to form a protective film by using chemical inhibitors. These inhibitors are fed into the cooling water and transported to the metal surfaces.

Several chemicals have been developed that will protect mild steel with a film so thin that it will not affect heat transfer. These chemicals are called corrosion inhibitors. Some work at the cathodes, some at the anodes. Corrosion inhibitors reduce or stop corrosion by interfering with the corrosion process. In practice, they usually affect either the corrosion cell anode or cathode.

The most logical corrosion preventive approach is to disrupt the cell. A corrosion cell consists of an electrolyte, an anode, a cathode, and a metallic path. One method involves imposing a nonconducting barrier (the film) between the metal and the electrolyte. This barrier can be a thin, adherent layer of scale on the metal surface, insulating it from the electrolyte, or it can be the product of the reaction between a corrosion inhibitor and the metal.

Anodic corrosion inhibitors, called passivators, interfere with the anodic reaction. If insufficient anodic inhibitor is present, the entire corrosion will concentrate at the unprotected area, which can cause severe pitting. Cathodic inhibitors, on the other hand, interfere with the cathodic reaction and reduce the corrosion rate in direct proportion to the reduction of the unprotected cathodic area. They are often referred to as blocking agents.



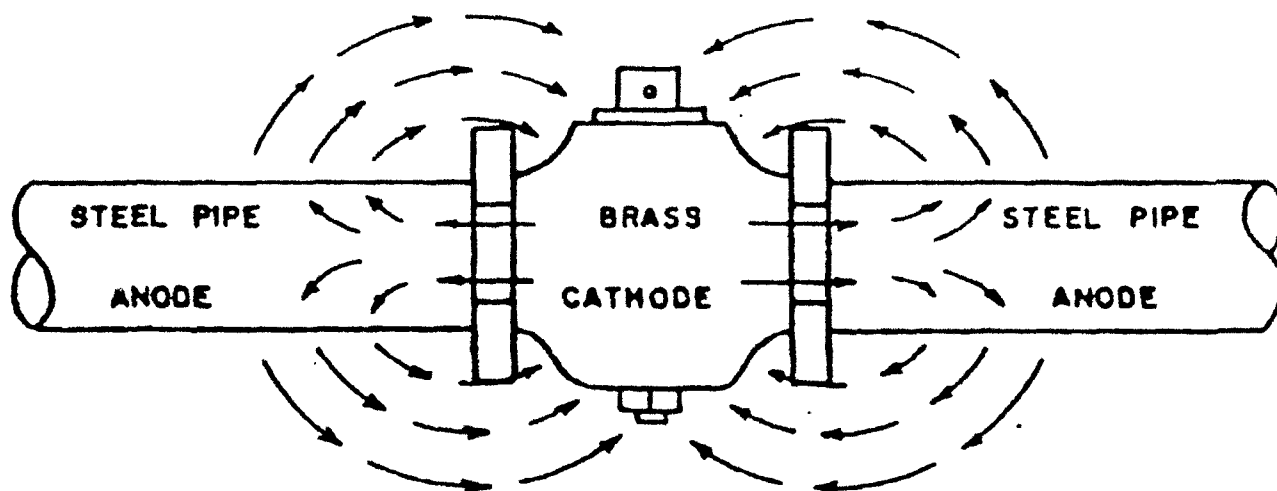


Figure 16. Galvanic Corrosion

#### D. ANODIC INHIBITORS

While they reduce the anodic areas available on metal surface, they are rarely able to eliminate all potentially corrosive regions. Since the reaction at the cathode is unrestricted, it provides a strong driving force, leading to rapid attack of the uninhibited anodic areas.

To illustrate the effect of this incomplete protection, consider a piece of steel in contact with uninhibited circulating water, losing metal evenly from its entire surface at a rate of 15 mils/yr (mpy). If we add an inhibitor that protects 90% of the surface, approximately the same total amount of metal (15 mpy) is lost from the unprotected 10% of the surface. This amounts to localized corrosion at a rate of 150 mpy, and takes the form of pitting.

Nitrites were the first anodic inhibitors introduced, and have been used in conjunction with polyphosphates. They must be used at levels above 500 ppm at pH above 7.5 to avoid pitting attack.

#### E. CATHODIC INHIBITORS

Cathodic inhibitors are generally considered "safe" inhibitors because they do not promote pitting attack. In general, they function by reducing the amount of cathodic surface area available to corrosive reaction by creating a tight, corrosion-resistant film on the metal surface.

In some cases, two or more cathodic inhibitors will form a tighter film than one alone; they can also be used in combination with anodic inhibitors for further protection. Incomplete protection does not cause local pitting, as it can at the anode, because the total reaction rate is proportional to the fraction of the cathodic area exposed.

Molybdates are used as cathodic inhibitors for mild steel. Applied alone, they require fairly high concentrations. For closed systems, levels of 100-200 ppm are needed to inhibit corrosion adequately.

See Table 4 for testing frequency.

TABLE 4. TESTING FREQUENCY AND REQUIREMENTS FOR CLOSED SYSTEMS

<u>System</u>	<u>pH</u>	<u>Sulfite</u>	<u>Nitrite</u>	<u>Molybdate</u>
HTW System	1/day	1/day		
H/W System	1/month		1/month	1/month
C/W System	1/month		1/month	1/month
Diesel System	1/month		1/month	1/month

## SECTION V

### CHILLED WATER SYSTEM

#### A. GENERAL

Protection of closed recirculating water systems generally features a high pH which is most often held between 8.5 and 9.5. Corrosion of mild steel is reduced substantially at high pH. However, systems with unresolved leaks can expect scale deposits if the hardness mineral content in the makeup water is high. Within this narrow pH range, the choice of corrosion inhibitor is more limited than for open systems.

The most common corrosion inhibitor for chilled water systems is referred to as boron nitrite. It uses borax as a buffering agent to maintain a pH above 8.5 and usually contains a variety of corrosion inhibitors that includes sodium nitrite, sodium nitrate, sodium silicate, and copper corrosion inhibitor.

Though rather effective, this treatment is not without shortcomings. Both the boron and nitrite are toxic to humans and cannot be used in food-processing plants. Nitrite is an excellent nutrient for bacteria growth. If bacteria enters this system, it can destroy the nitrite, produce low pH levels, and produce slime deposits as well. Finally, if air enters the system at points such as pump seals, nitrite converts to nitrate, which is not as effective for corrosion control.

Molybdate-based treatments have found recent use with considerable success. They often contain copper corrosion inhibitors and occasionally an alkali buffering agent to maintain pH above 8.0. The molybdate is maintained at levels of 100-200 ppm (as  $\text{MoO}_4$ ). This treatment is not toxic, is environmentally acceptable, and does not contribute to biological growth.

#### B. TREATMENT PROGRAM FOR CHILLED WATER SYSTEMS

##### 1. Nitrite-Borax.

- a. Soften makeup water if hardness is over 250 ppm as  $\text{CaCO}_3$ .
- b. Maintain 600-1000 ppm as  $\text{NO}_2$ .
- c. Add sodium carbonate to maintain a pH range of 8.5 to 9.5.
- d. Prevent degradation of nitrite, supplement with a biocide.

## 2. Molybdate-Caustic Soda.

- a. Soften makeup water if hardness is over 250 ppm as  $\text{CaCO}_3$ .
- b. Maintain 100 to 125 ppm molybdate as  $\text{MoO}_4$ .
- c. Add sodium hydroxide to maintain a pH range of 8.0 to 9.0.

## C. TREATMENT EVALUATION

The effect of a problem may not be easily traced to the cause. Only when the system is very sensitive to a slight deposition on the heat transfer surface is it possible to see the effect. If the conditions are right, a layer of slime can start growing, followed by infection by anaerobes under the slime-forming bacteria. Several weeks or months later, pits may show up in the heat exchanger.

Most monitoring methods are designed to reveal problems before they cause severe damage. The information obtained from corrosion monitoring depends on the methods used. The traditional and most common method used in a closed system is corrosion coupons.

The coupon concept involves immersion of a metal specimen of the same metallurgy as found in the system. Each coupon is preweighed and has a known surface area. After the testing period is completed, the coupon is cleaned and reweighed. The difference between the two weights represents the amount of metal lost during the testing period. The corrosion rate is traditionally reported as mils per year (mpy).

Typical test period is 30 days for low corrosive waters, but some experts recommend at least 90 days. One of the reasons for lengthy periods is to minimize the rapid corrosion undergone by the coupons in their first few days of exposure. Since the information from the coupon reflects cumulative corrosion effects in the system, it cannot identify daily upsets.

## D. GUIDELINE FOR ACCESSING CORROSION

A guideline for assessing corrosion rates of common metals is listed below. These rates and comments assume general system corrosion. Pitting, however, is the primary cause of equipment failure, and any indication of its presence should be investigated (See Table 5).

TABLE 5. GUIDELINE FOR ASSESSING CORROSION

<u>Metal</u>	<u>Corrosion rate mils/yr</u>	<u>Comment</u>
Carbon steel	0-2	Excellent corrosion resistance
	2-3	Generally acceptable for all systems
	3-5	Fair corrosion resistance; acceptable with iron fouling-control program
	5-10	Unacceptable corrosion resistance: Migratory corrosion products may cause severe iron fouling
Admiralty brass	0-0.2	Generally safe for heat exchanger tubing and mild steel equipment
	0.2-0.5	High corrosion rate may enhance corrosion of mild steel
	above .5	Unacceptable high rate for long term; significantly affects mild steel corrosion
Stainless steel	0-1	Acceptable
	above 1	Unacceptable corrosion resistance

The involvement of the coupon test must be understood to evaluate the system corrosion rates. The coupon is not a heat transfer surface; therefore, the corrosion rate of a heat transfer surface may be greater than that of the coupon. An evaluation of the system corrosion rate during operation requires a heat transfer specimen with the same metallurgy as the heat exchanger.

#### E. CHECKLIST AND CALCULATIONS FOR CLOSED SYSTEMS

##### 1. Minimize makeup rate

a. Makeup rate greater than 5% of the system's volume annually is intolerable.

##### b. Inspect for leaks at the following sources:

- (1) Expansion tanks
- (2) Multiple makeup water connections
- (3) Faulty valving or design at makeup station
- (4) Air eliminators
- (5) Connections with other piping systems
- (6) Pump seals

c. Keeping makeup low prevents hard water, high dissolved salts, and oxygen from entering the system.

2. Prevent potable water contamination

a. Installing backflow preventers or air gaps on makeup.

b. Installing these before chemical treatment begins.

c. Eliminating any bypass loop around the backflow preventer.

3. Determining system's capacity

The following procedures can be used to determine the system's capacity in 1000 gals increments. Once the system's size is calculated, the initial chemical dosage can be estimated.

a. Make sure that all leaks in the system have been eliminated.

b. Measure the initial chloride content in the circulating water.

c. Add a box of household Morton Salt (1.625 lbs) to the system.

d. Allow the solution to circulate for approximately 24 hours.

e. Measure the adjusted chlorides content in the circulating water.

f. System's capacity in 1000 gals. Increments are equal to 117 divided by the total chlorides minus the initial chlorides.

EXAMPLE: If the initial chloride content in the system is 145 ppm as Cl and the adjusted chloride content is 210 ppm as Cl, the system's capacity is calculated as follows:

$$\text{Capacity in 1000 gals increments} = \frac{117}{210 - 145}$$

$$\frac{117}{65} = 1.8 \times 1000 \text{ gals}$$

System's capacity is 1800 gals.

#### 4. Estimating initial chemical dosage for a closed system

Prior to estimating the initial dosage, the analyst needs knowledge of the approximate water capacity in the system, the percent of the treatment chemical active ingredient, and the desired ppm. Parts per million (ppm) is the ratio of weight of a chemical to the weight of one million gallons of water. The following is the formula for calculating initial dosage in pounds to obtain a desired ppm.

$$\frac{(C/10^6) (8.3) (V)}{R} = \text{lbs of treatment chemicals}$$

Where  $10^6 = 1,000,000$

C = desired ppm expressed as a ratio to 1,000,000

(100 ppm = 100/1,000,000)

8.3 lbs = the weight of one gallon of water

V = system's capacity in gallons

R = % (expressed as a decimal) of the desired  
chemical by weight of the total additive

Note: 1 ppm = 8.3 lbs/ $10^6$

Example: A closed water system contains 1800 gals.  
The active sulfite ingredient is 96%.  
The desired sodium sulfite concentration is  
100 ppm.

$$\frac{(100/10^6) (8.3) (1800)}{96\%} = 1.5 \text{ lbs to 1800 gals}$$

#### 5. Determining leaks in a treated system

a. Measure the inhibitor concentration once per month.

b. More than 2% loss in less than 4 months is excessive.

c. EXAMPLE: The molybdate concentration in chilled water system is 125 ppm, 3 months later the concentration is 123 ppm, and at the end of 4 months the concentration has decreased to 122 ppm. What is the percent of water loss?

$$\text{Loss} = \frac{\text{Initial} - \text{Final}}{\text{Initial}}$$

$$\text{After 3 months } \frac{125 \text{ ppm} - 123 \text{ ppm}}{125 \text{ ppm}} = 1.6\%$$

$$\text{After 4 months } \frac{125 \text{ ppm} - 122 \text{ ppm}}{125 \text{ ppm}} = 2.4\%$$

To preclude the system leakage calculation above, a water meter should be installed in the makeup water line of the system. The reading should be recorded and compared with all subsequent readings.



SECTION VI  
OPEN RECIRCULATING COOLING WATER SYSTEM

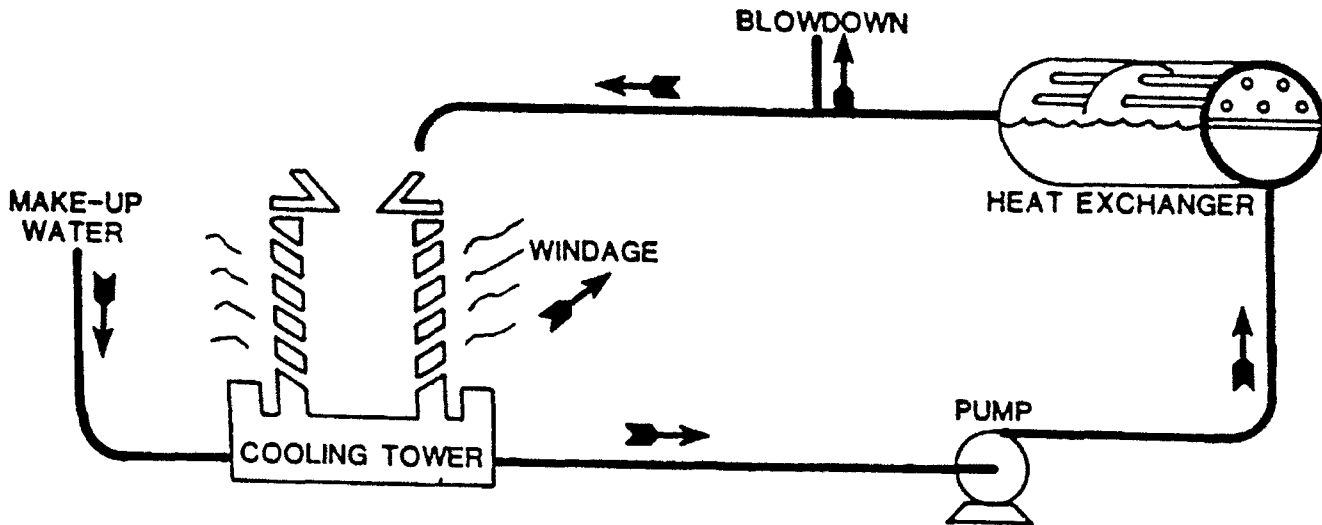


Figure 17. Typical Cooling Tower Operation  
(Courtesy of Puckorius & Associates)

**A. GENERAL**

An open recirculating system is one type of cooling water system designed to absorb heat from one area and reject it at another area. The water absorbs heat at the refrigeration condensing units, and rejects the heat at the atmosphere at the cooling tower (See Figure 17).

A cooling tower is a component in the system for cooling water by bringing it in contact with air. Heat is released from the water by conduction (the transfer of heat from the warm water to the cool air), and evaporation.

**B. TYPES OF COOLING TOWERS**

Natural Draft Towers achieve air flow without the use of fans. Air flow across the falling water depends on the wind conditions. The dense spray improves efficiency by bringing more water drops in contact with air.

Forced Draft Towers use one or more fans to blow air up through the tower fill against the flow of falling water. Drift eliminators are installed to prevent water entrained in the air from leaving the system.

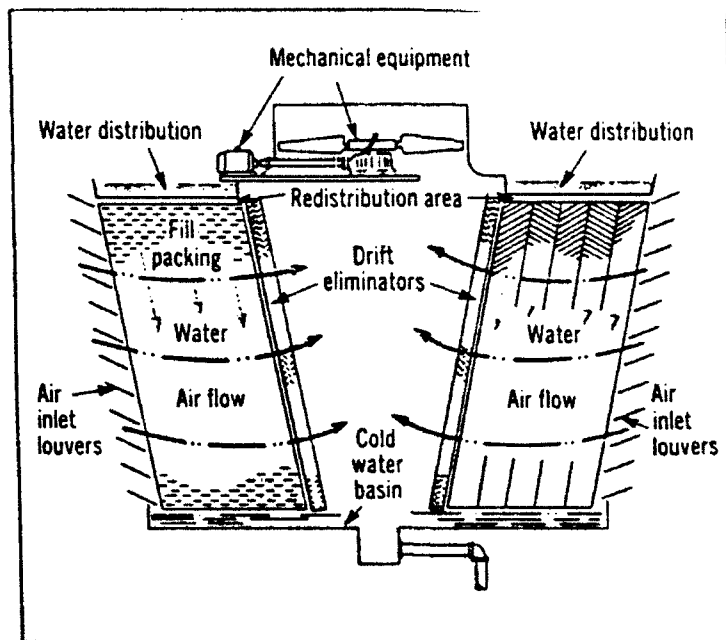


Figure 18. Induced Draft Cooling Tower

Induced Draft Towers use one or more fans to draw air across the falling water drops. The air flows either cross-flow or counter flow to the falling water drops (See Figure 18).

### C. COOLING TOWER OPERATION

The recirculating water is pumped to the tower distribution deck. The distribution system dispenses the water evenly over the tower fill (See Figure 19). As water flows down the cellular fill toward the tower sump, the water spreads out into a thin film where the air can effectively cool the entire film. For wood slat fill, water droplets bounce from one layer of wood to another, the air cools the outside of each water drop. Water distributed by the spray method is discharged from the spray nozzles in small droplet form. Air is blown across the droplets and by evaporation, heat is rejected to the atmosphere. The water collects in the tower sump and the cooling operation is repeated. As a result of evaporation, the mineral content in the circulating water is concentrated. A portion of the water must be bled off to control the mineral concentration in the circulating water. Makeup water must be added to replace the water lost due to evaporation, bleed off, and leaks.

Although the temperature of the recirculating cooling water is much lower when compared to a boiler operation, the aeration and continuous exposure of the water in the system to air promotes both scale and corrosion. For this reason an open recirculating system has the greatest potential for all types of water related problems.

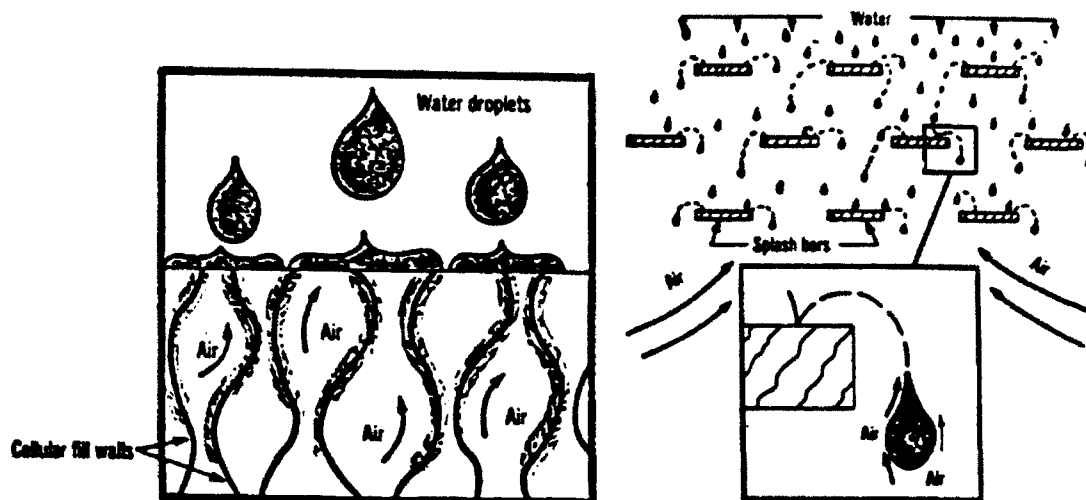


Figure 19. Cooling Tower Fill Provides Cooling Effect as Water Flows From the Distribution Deck to Tower Sump.

#### D. DETERMINING WATER QUALITY

Knowing the water quality is an essential element in determining the type of treatment needed for a recirculating cooling water system. Prior to embarking on a water treatment program for a recirculating cooling system, the makeup water should be analyzed to determine its potential for scaling or corrosive effect in the system.

The pH of Saturation ( $pH_s$ ) is the pH at which the calcium carbonate solubility is constant under a specific water condition. This requires the knowledge of the following:

1. Calcium hardness (as  $CaCO_3$ )
2. Total alkalinity (as  $CaCO_3$ )
3. Total dissolved solids
4. Temperature (max at heat exchanger)

See Table 6 for calculating the  $pH_s$ .

The Langelier Saturation Index (LSI) is a method used to predict the scaling or corrosiveness of potable water used as makeup water for an open recirculating system. The LSI equates to the actual pH of the water minus its pH of saturation ( $pH_s$ ) for calcium carbonate ( $pH - pH_s$ ). If the index is positive, there is a potential for calcium carbonate to produce scale. If the index is negative, the potential for scale deposition is reduced and the corrosive potential increases. The water becomes more scale depositing as the number increases on the positive side of the spectrum and more corrosive as the number increases on the negative side of the spectrum.

TABLE 6. CALCULATION OF CALCIUM CARBONATE SATURATION INDEX

A			C		D	
TOTAL SOLIDS mg/L	A		CALCIUM HARDNESS mg/L CaCO <sub>3</sub>	C	M.O. ALKALINITY mg/L CaCO <sub>3</sub>	D
50 - 300	0.1		10 - 11	0.6	10 - 11	1.0
400 - 1000	0.2		12 - 13	0.7	12 - 13	1.1
B			14 - 17	0.8	14 - 17	1.2
TEMPERATURE			18 - 22	0.9	18 - 22	1.3
°C	°F	B	23 - 27	1.0	23 - 27	1.4
0-1	32-34	2.6	28 - 34	1.1	28 - 35	1.5
2-6	36-42	2.5	35 - 43	1.2	36 - 44	1.6
7-9	44-48	2.4	44 - 55	1.3	45 - 55	1.7
10-13	50-56	2.3	56 - 69	1.4	56 - 69	1.8
14-17	58-62	2.2	70 - 87	1.5	70 - 88	1.9
18-21	64-70	2.1	88 - 110	1.6	89 - 110	2.0
22-27	72-80	2.0	111 - 138	1.7	111 - 139	2.1
28-31	82-88	1.9	139 - 174	1.8	140 - 176	2.2
32-37	90-98	1.8	175 - 220	1.9	177 - 220	2.3
38-43	100-110	1.7	230 - 270	2.0	230 - 270	2.4
44-50	112-122	1.6	280 - 340	2.1	280 - 350	2.5
51-55	124-132	1.5	350 - 430	2.2	360 - 440	2.6
56-64	134-146	1.4	440 - 550	2.3	450 - 550	2.7
65-71	148-160	1.3	560 - 690	2.4	560 - 690	2.8
72-81	162-178	1.2	700 - 870	2.5	700 - 880	2.9
			800 - 1000	2.6	890 - 1000	3.0

1. Obtain values of A,B,C and D from above table.

2.  $pH_s = (9.3 + A + B) - (C + D)$ .

3. Saturation Index =  $pH - pH_s$ .

If index is 0, water is in chemical balance.

If index is a plus quantity, there is a tendency for calcium carbonate deposition.

If the index is a minus quantity, calcium carbonate does not precipitate, and the probability of corrosion (if dissolve oxygen is present) will increase with an increase in the negative value of the index.

To determine temperature at which scaling begins (i.e.,  $pH = pH_s$ ), find the temperature equivalent to the following value of B:

$$B = pH + (C + D) - (9.3 + A)$$

$$\text{Ryznar Stability Index} = 2(pH_s) - pH$$

With water having a Stability Index of 6.0 or less, scaling increases and the tendency for corrosion decreases.

When the Stability Index is above 7.0, a protective coating of calcium carbonate may not be developed.

The Ryznar Stability Index (RSI) is another method used to predict the scaling or corrosiveness of potable water used as makeup water for an open recirculating system. The RSI equates to  $2\text{pH}_s - \text{pH}$ ; the value for the RSI is always positive. Water having a stability index of 6.0 or less has a potential for scale deposition. An index of 7.0 and higher represents an increase in the potential of corrosion. Values between 6.0 and 7.0 are considered neutral.

The RSI and the LSI can only be used to predict the potential for scale deposit or corrosion. Once the water enters the system, it is exposed to conditions that can alter the predicted characteristic. For example, the makeup water for a cooling system has an LSI of -0.2 and an RSI of 7.9, which indicates corrosive tendency. However, when this same water enters the cooling system and cycles up, the LSI shifts to +1.8 and the RSI drops to 5.2, which indicates scaling tendency.

When chemicals are used to prevent scale deposition, the indices will still predict scaling tendency but the water can actually be corrosive. The cooling tower water always contains dissolved solids and dissolved oxygen which contribute to the corrosion no matter what the indices predict. It is always safe to assume that corrosion is eminent, and corrosion inhibitors should be used to protect mild steel and copper alloys.

#### E. FACTORS THAT INFLUENCE CORROSION

A number of characteristics in a cooling system can influence the amount and rate of corrosion that will occur. The most important ones are:

1. Oxygen content
2. Total solids (dissolved and suspended)
3. Degree of alkalinity or acidity
4. Water velocity
5. Temperature
6. Microbial growths

Dissolved oxygen accelerates the corrosion rate. Dissolved solids will affect the corrosion reaction by increasing the electrical conductivity of the water. The more dissolved solids, the higher the conductivity and the greater the corrosion. High concentrations of dissolved chlorides and sulfates are particularly corrosive in a cooling system.

Suspended solids influence corrosion by eroding or abrading the metal surface. They can also create deposits, which form localized corrosion cells. Acidity and low alkalinity promote corrosion by increasing both the dissolution rate of the base metal and the oxide-film formation on the metal surfaces. Surprisingly, even neutral pH (7.0) or slightly alkaline pH (7.5) can be corrosive.

Water flow increases corrosion by bringing oxygen ( $O_2$ ) to the metal and carrying away corrosion products. High velocity, in excess of 5 feet per second (fps), erodes the protective oxide film on the metal surface. Continued stripping of the oxide film as it reforms causes the metal to wear thin. When water velocity is low, flowing less than 5 fps, suspended solids deposit and enhance corrosion by establishing local corrosion cells.

Temperature will cause corrosion rates to double with every 25-50 degree rise up to 160°F. Both temperature and acidity affect the corrosion effect of cooling water on metal. Microbial growth promotes formation of corrosion cells. Moreover, the by-products of some organisms and the organisms themselves promote corrosion.

#### F. TYPES OF CORROSION

General attack is a term that describes the uniform distribution of corrosion over an entire metal surface (show slide). The large amount of iron oxide produced through general attack contributes to the severe fouling problem.

Localized or pitting attack occurs when isolated metal areas are corroded. Pitting is the most serious type of corrosion because all the corrosive action is concentrated in a very small area. Pitting attack can cause metal to perforate in a very short time.

Galvanic attack occurs when two different metals are in physical contact. In such a case, the more active metal corrodes rapidly. Common examples in a water system are steel and brass, aluminum and steel, zinc and steel, and zinc and brass. In each case, the first metal of the pair will corrode. A simple example of galvanic corrosion between two dissimilar metals is a steel pipe screwed into a bronze valve or copper tubes joined to a mild steel tubesheet in a heat exchanger.

#### G. PURPOSE FOR COOLING WATER TREATMENT

Water treatment for an open recirculating system can be challenging even for the most knowledgeable analyst. A treatment program developed for this system must provide for control of scale deposits, corrosion, microbial growth, and fouling.

Chemical selection is important because not only must it meet a specific need, but it must also be compatible with any other chemical in the system. For example, polyacrylate, a dispersant used to control scale in the system is rendered ineffective when a biocide is added to control biological growth.

Corrosion occurs in open recirculation systems as a result of low pH, corrosion deposits, microbial byproducts, and airborne contaminants that deposit in the system. Destruction of costly equipment, decrease in efficiency/capacity, considerable downtime, and costly production losses are all known to be the direct result of corrosion. Corrosion control in the open recirculating system can be accomplished by adjusting the pH to maintain the water on the alkaline side. Corrosion inhibitors are necessary to disrupt and prevent the formation of corrosion cells on the metal surfaces. Microbial by-products and airborne contaminants can be kept in suspension with a dispersant and later removed by blowdown to prevent the development of any corrosion cells.

Overemphasis on corrosion control can lead to problems of another kind, scale deposit. If the makeup water indices predict scaling potential, a treatment program must be developed to control deposition in the system. The primary factors that contribute to scale deposition are pH (alkalinity), mineral content, and temperature. The rate of calcium carbonate scale deposit increases in direct proportion to an increase of temperature and pH. Scale deposition on the heat exchanger tubes reduces the condensing unit efficiency/capacity and leads to unscheduled maintenance. Chemicals have been developed that will keep hardness minerals in suspension or alter the mineral structure to prevent deposition. Blowdown is also necessary to prevent super saturation. Electronic or magnetic devices for scale control have not been proven effective and should not be used.

Fouling is categorized as either biological or nonbiological. Biological foulants are living matters like algae, bacteria, and fungi. Nonbiological foulants are nonliving matters such as silt (airborne contaminants), corrosion products, and microbiological by-products. The rate of fouling is influenced by the water quality, air quality, water velocity, and temperature. Heat exchangers are more susceptible to fouling because of the filtering action of the tubes in a confined space. Fouling of the heat exchangers can lead to reduction of heat transfer and can be the starting point for a corrosion cell to develop (See Figure 20).

Biological fouling in a cooling water system can be troublesome and costly. It usually shows up in the form of bacteria, fungi, and algae. Microbiological contaminants enter the system in the makeup water or by being scrubbed from the air passing through the cooling tower.

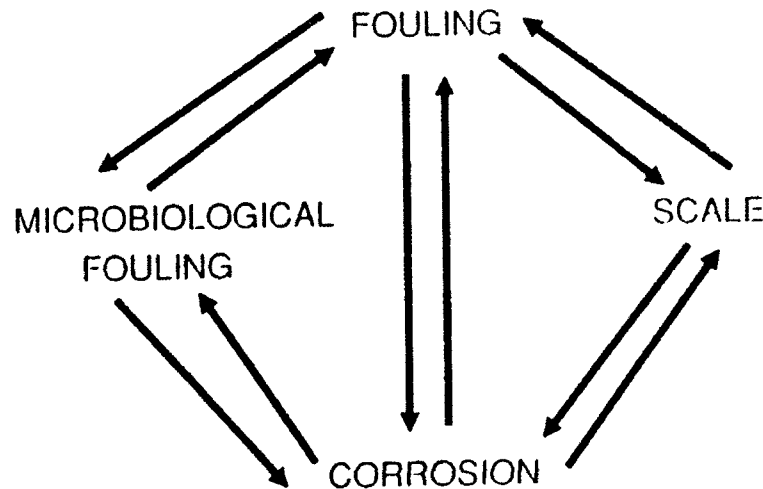


Figure 20. Fouling Contributes to Other Problems Encountered in the System.

A cooling tower system provides the perfect environment for microbiological growth. The system provides the right temperature and the presence of organic and inorganic salts ensures plenty of nutrients.

Several groups of bacteria produce acids and waste products that readily attack metal surfaces. They can produce elaborate profuse gelatinous capsules, which are sticky and can accumulate mud and other debris into masses that clog screens and impede circulation in the heat exchanger.

Fungi are simple plants without chlorophyll. Approximately 10% of all fungal groups utilize wood as a nutrient source. This results in the destruction of the cooling tower wood.

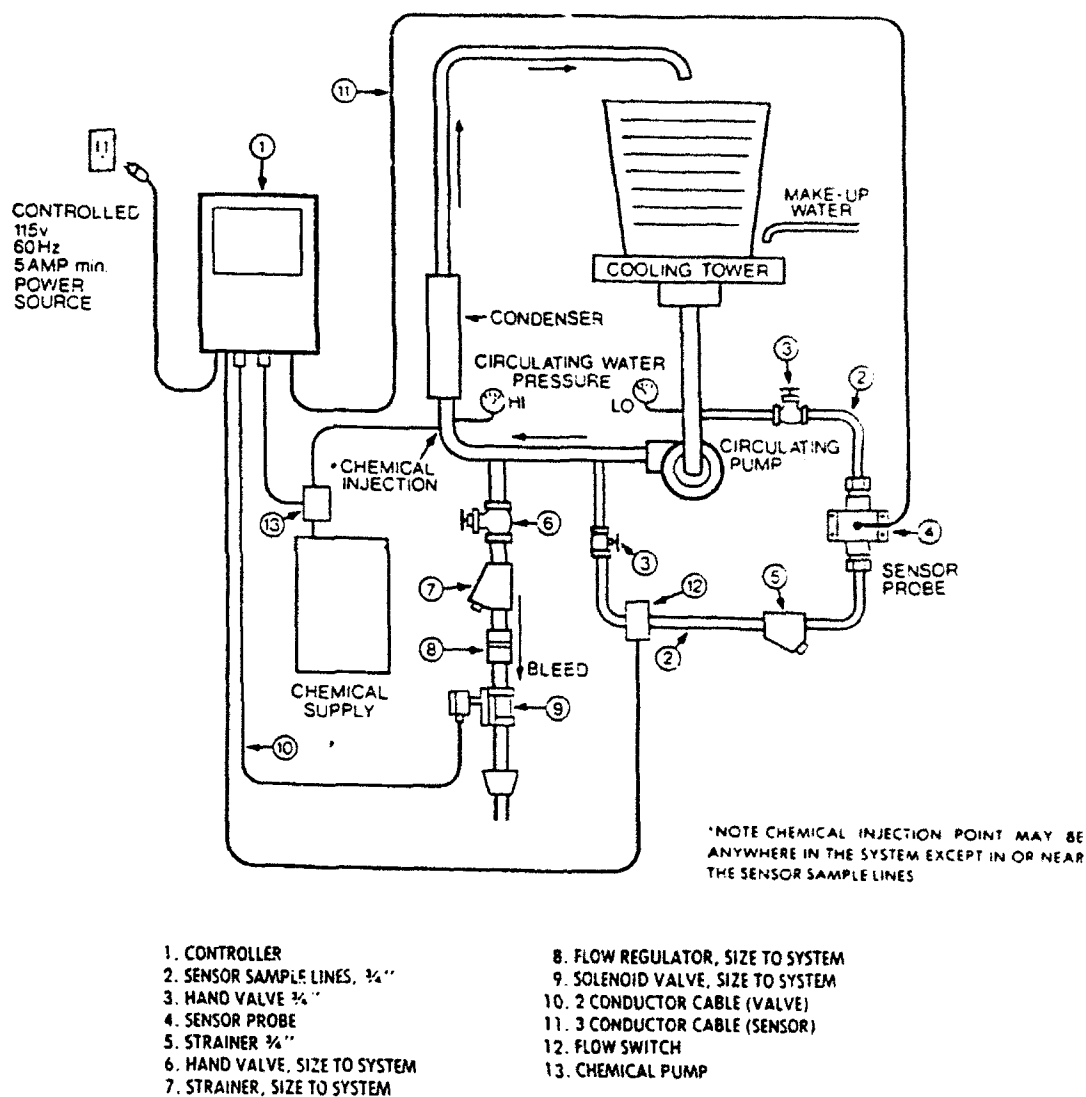
Algae is a simple aquatic plant that requires air, water, and sunlight for its survival. The distribution deck and the side walls of the cooling tower provide all three. Although ordinarily less troublesome than bacteria, algae also secretes a sticky sheath similar to the slime layer in bacteria.

Nonbiological fouling deposits may originate from airborne contaminants, corrosion products, decayed wood fibers, or chemicals added to the system. Deposits in the system occur largely because of low water velocity, size of the particulate, and the water viscosity. Fouling results in decreased efficiency of the heat exchanger, flow restriction, and increased corrosion rate.

#### H. COOLING WATER TREATMENT METHODS

Chemical feed and monitoring equipment are essential for an effective water treatment program. Using automatic feed equipment increases the reliability of the treatment program. (See Figure 21).





**Figure 21. Automatic Chemical Feed System**

As the water in the tower evaporates, minerals are left behind. These minerals increase the water electrical conductance; the conductivity controller senses this increase and opens a bleed valve. As water bleeds from the system, makeup water is added which dilutes the solids content in the tower water. The controller senses this dilution and closes the bleed valve. The chemical feed pump is energized during blowdown to replace the treatment chemical lost.

#### 1. Corrosion Control

One approach for preventing corrosion is forming a protective film by using chemical inhibitors, which are fed into the cooling water and transported to the metal surfaces.

# ELECTROLYTE

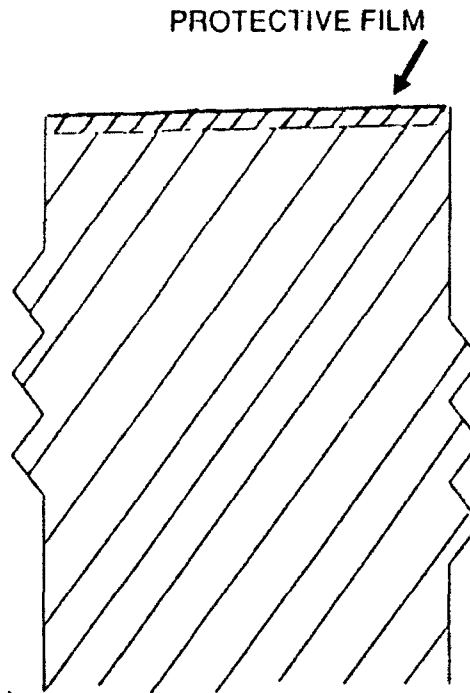


Figure 22. Corrosion Inhibitor Protective Film

Since an electrochemical cell is necessary for corrosion, the most logical preventive approach is to destroy or disrupt the cell. One method involves imposing a nonconducting barrier between the metal and the electrolyte (See Figure 22). This barrier can be a thin, adherent layer of scale on the metal surface, insulating it from the electrolyte, or it can be the product of the reaction between a corrosion inhibitor and the metal. Several chemicals have been developed that will protect mild steel with a film so thin that it will not affect heat transfer.

Corrosion control in open recirculation systems involves basically the same principals applied to the closed recirculating systems. The only difference is that the open recirculating system requires constant monitoring due to water loss as a result of evaporation and blowdown. When water is added to make up for the loss, treatment chemical(s) needs to be injected into the system. Chemicals designed to inhibit corrosion are added to passivate the metals in the system. It is important that the cooling water system be free from any type of foulant deposits. Corrosion inhibitors are not very effective if the foulants deposit on the metal surface. In fact, corrosion is enhanced at these areas because the inhibitors cannot come in contact with the metal surface.

Corrosion is also controlled by allowing the cycle of concentrations (COC) to increase in the system or by controlling the pH of the circulating water.

## 2. Scale Control

When a system is allowed to cycle up to prevent corrosion, the condition is often ideal for scale deposition. Solubilizing chemicals such as chelants and inorganic phosphates have been used to keep scale forming minerals in solution. However, polymeric organic and organic phosphorus compounds have been developed that have virtually replaced chelants and inorganic phosphates. Polyacrylates are the most popular polymeric organic used for calcium based scale control. They are not affected at high temperatures and do not degrade easily. Polyacrylates remain stable and soluble at various pH levels, but its use is not without shortcomings. The main disadvantage is that biocides and flocculants in the circulating water may remove the polyacrylate from solution and reduce its ability to control scale.

Phosphonates are the most commonly used organic phosphorus compound for calcium scale control in recirculating cooling water systems. HEDP (1-hydroxy-ethylidene-1,1-diphosphonic acid) and AMP (amino-methylene phosphonic acid) are the two most frequently used phosphonates. HEDP is the preferred phosphonate. Unlike AMP, it remains stable in the presence of chlorine. But it too is not without disadvantages; HEDP will degrade in the presence of iron and lose its scale controlling ability. Steel and copper corrosion inhibitors should be used in conjunction with either phosphonate because HEDP and AMP are known to attack steel and copper alloys. Chemical application should be continuous and uniform. Severe scaling will result if the treatment chemical(s) is lost or if there is an interruption of the chemical feed. The last method of scale control is to use a crystal modifier. A crystal modifier allows scale to form but distorts the crystal structure which prevents an adherent scale formation. The altered structures form a nonadherent sludge that can be kept in solution until removed during blowdown or side-stream filtration. Turbidity in the cooling water indicates that the crystal modifiers are taking effect. The major advantage of crystal modifiers is that they allow the system to operate at higher cycles of concentration than with solubilizing chemicals.

Although solubilizing chemicals and crystal modifiers allow the system to operate at a higher COC, the limiting factor for COC should be based on the maximum allowable silica content in the recirculating water. The solubility of silica is not influenced by any chemical on the market today. To prevent silica scale deposition, the silica content in an open recirculating cooling water system should not exceed 150 ppm.

### 3. Foulant Control

Identifying the type of foulant is the first step in solving or preventing fouling problems. This information will help to identify the source of the foulant and aid in selecting the appropriate treatment program. If the deposit composition and characteristics are not known, the choice of treatment can be no better than an educated guess.

Fouling control requires the addition of dispersant chemicals that will keep the foulant in suspension until it is carried away with the blowdown. Dispersants impart like charges on the particles which modify the surface to an extent that surrounding particles are repelled.

Another approach to control fouling type deposition is to use a flocculant polymer. This product is designed to promote the formation of a light fluffy floc which is removed through blowdown or a side-stream filter.

### 4. Microbiological control

Microbiological contamination in the open recirculating system can lead to fouling of the system and all the associated problems. The presence and growth of these organisms can be controlled by any three of the following methods: mechanical, thermal, and chemical.

The mechanical method focuses primarily on prevention of organisms entering the system. Types of mechanical methods include trash bars, rakes, and strainers in various designs, combinations, and sizes.

The thermal method is only effective for certain types of organisms. It involves raising the temperature above 105°F for at least two hours. This method must be done frequently enough to kill the organisms in its juvenile stage, and its effectiveness depends on their acclimation temperature.

Chemical treatment is the third and most established method for microorganism control. There are a variety of ways in which microbiocides function to inhibit microorganism growth. Some chemicals alter the permeability of microbe cell walls, thereby interfering with its vital life process. The first choice in biological treatment is whether to use oxidizing or nonoxidizing chemicals. The choice usually depends on limitation on discharge of toxic substances, temperature, pH, system operating parameters, and the system design.

Chlorine is one of the most familiar and effective industrial oxidizing biocide. When chlorine enters the water, it decomposes to form hydrochloric and hypochlorous acid. Hypochlorous acid has the biocidal effect as it easily diffuses through the microorganism cell wall.

Chlorine inhibits the critical cellular process necessary for microbial respiration. Generally, pH levels of 6.5 to 7.5 are considered practical for chlorine-based microbial control program. Other oxidizing agents available for microbial control are chlorine dioxide and brominated propionamides.

Nonoxidizing biocides such as organo-tin compounds are known for their toxicity to algae, molds, and wood-rotting organisms. They penetrate an organism's cell wall and disrupt essential life sustaining protein groups. Other nonoxidizing biocides that are available are quaternary ammonium salts which kill by decomposing cells; organo-sulfur which is highly effective against fungi and slime forming bacteria; methylene bis-thiocyanate which inhibits the transfer of electron in the microorganism and results in cell death; isothiazolinone which is useful to combat a wide spectrum of microorganisms at a wide pH range and is considered by some to be the best algicide on the market. Nonoxidizing biocides are often used in conjunction with oxidizing biocides for a broader control.

Microbiocides are occasionally fed into a system on a continuous basis, however, slug feeding is often preferred for a rapid, effective population reduction. The biocides should be alternated periodically to prevent organisms immunity.

## I. CONCLUSION

Water treatment for industrial systems is a vital part of the overall maintenance program. An effective treatment program will greatly enhanced equipment integrity, reliability, and life expectancy. Developing and maintaining an effective water treatment program for heating and air conditioning systems will reap rewards that could extend beyond base level operation to higher AF echelons.

## **APPENDIX A**

### **DEFINITIONS**

## DEFINITIONS

**ACID** - A compound, usually having a sour taste, which is able to neutralize an alkali or base; a substance that dissolves in water with a formation of hydrogen ions.

**AERATION** - The bringing about of intimate contact between air and liquid by one of the following methods: spraying the liquid in the air; bubbling air through the liquid; or by agitation of the liquid to promote surface absorption of air.

**AEROBIC** - Bacteriological life which requires the presence of air for growth and life cycle.

**ALGAE** - Tiny plant life, usually microscopic, existing in water. They are mostly green, blue-green, or yellow-green and are the cause of most tastes and odors in water. They create suspended solids when they grow in an industrial water system.

**ALKALINITY** - (a) A term used to represent the content of carbonates, bicarbonates, hydroxides, and occasionally borates, silicates, and phosphates in water. (b) The capacity of water to react with hydrogen ions.

**ALKALINITY, TOTAL OR MIXED INDICATOR (M)** - A measure of the total alkalinity of water. Measured by the quantity of 0.02 N sulfuric acid required to bring water to pH of 4.4, as indicated by the change in color of mixed indicator. Results are expressed in parts per million (ppm) as calcium carbonate.

**ALKALINITY, PHENOLPHTHALEIN (P)** - A measure of hydroxide ions (OH) plus one-half of the normal carbonates in water. Measured by the quantity of 0.02 N sulfuric acid required to bring the water to pH 8.2, as indicated by the decolorization of phenolphthalein indicator. Results are expressed in parts per million (ppm) as calcium carbonate.

**ALKALINITY, HYDROXYL** - A measure of hydroxyl ion (OH<sup>-</sup>) contribution to the alkalinity. This is related to the system pH and also may be referred to as causticity.

**ANAEROBIC** - Bacteriological life which does not require air for growth. Air is a poison to these bacteria.

**BACKFLOW PREVENTER** - A device for a water supply pipe to prevent the backflow of treated water into the water supply system.

**BACKWASH** - The reversal of flow through a filter or an ion exchanger to wash clogging material out of the filtering medium and reduce conditions causing loss of head.

**BACTERIA** - Simple single-cell microscopic organisms generally free of pigment. They do not require light for their life processes.

**BASE** - An alkali or hydroxide of the alkali metals and of ammonia. They can neutralize acids to form salts and water. A base will ionize to form hydroxyl ions ( $\text{OH}^-$ ).

**BIOCIDES** - Material typically used to destroy microorganisms (also called microbiocides).

**BIOLOGICAL DEPOSITS** - Water-formed deposits of organisms or the products of their life processes. Biological deposits may be composed of microscopic organisms, as in slimes, or of macroscopic organisms, such as barnacles or mussels.

**BLOWDOWN** - The action of draining a portion of water from a system to reduce the concentration of dissolved solids or to discharge accumulations of materials carried by the water.

**BRINE** - A saturated solution for ion exchange regeneration, refrigeration, or cooling processes. It is usually a sodium chloride solution for ion exchange regeneration. It may be sodium chloride or calcium chloride for refrigeration.

**CAUSTICITY** - A common term that describes hydroxyl alkalinity or the alkalinity resulting from presence of the hydroxyl ion ( $\text{OH}^-$ ).

**CONCENTRATION** - A measure of the amount of dissolved substances contained per unit volume of solution. May be expressed as grains per gallon (gpg), pounds per million gallons (lb/mil gal), milligrams per liter (mg/l), or parts per million (ppm).

**CONDENSATE** - The material formed when vapor returns to the liquid state. In steam heating systems, the water condensed from steam. In air conditioning, water extracted from air as by condensation on the cooling coil of a refrigeration machine.

**CONDUCTIVITY, ELECTRICAL** - The reciprocal of the resistance in ohms measured between opposite faces of a centimeter cube of an aqueous solution at a specified temperature. Electrical conductivity is expressed in micromhos ( $\mu\text{mho}$ ). This is used as a measure of total dissolved solids.

**CORROSION** - The destruction of a substance, usually a metal, or its properties because of a reaction with its (environmental) surroundings.

**CYCLE OF CONCENTRATION** - The ratio of any one or all of the minerals in the source of water to that in the system water. This is obtained by dividing the system water mineral concentrations by the source water mineral concentrations.



**DEAERATOR** - Device for removing noncondensable gases from the boiler. These may operate on the principle of either heat or vacuum.

**DEALKALIZATION** - Exchange of bicarbonate for chlorides in an ion exchange process.

**DEIONIZATION** - Complete removal of ions from water.

**DEMINERALIZATION** - Reduction of the mineral content of water by a physical or chemical process; removal of salts.

**DISINFECTION** - The process of killing most (but not necessarily all) of the harmful and objectionable microorganisms in a fluid by various agents such as chemicals, heat, ultraviolet light, ultrasonic waves, or radiation.

**DISPERSANT** - Chemicals added to water systems to keep insoluble solids suspended or dispersed. Dispersants are used to prevent accumulation of deposits or sludge.

**DISSOLVED SOLIDS** - (a) Solids, usually minerals, that are present in solution. (b) The dried residue from evaporation of the filtrate after separation of suspended solids.

**EVAPORATION** - The process by which water passes from a liquid state to a vapor. It is the main process by which heat is removed from a cooling tower and steam produced in a boiler.

**FEEDWATER** - Water being applied to the feedwater heater or to the boiler. This consists of both makeup and condensate return.

**FILMING AMINES** - Chemicals that form an impervious barrier between metal and the steam condensate to prevent corrosion.

**FOULANTS** - Deposition of materials normally in suspension. This includes such things as silt, air scrubbed dust, microbiological residuals, reaction products from treatment, and corrosion products.

**GENERIC CHEMICALS** - A chemical identified and purchased by the recognized chemical name such as the International Union of Pure and Applied Chemistry (IUPAC) designation. These generic chemicals may be blended or used separately. They are usually much less expensive than special chemical blends developed by manufacturers under a trade name.

**HARDNESS** - (a) A characteristic of water, chiefly due to the existence of carbonate and sulfate (and occasionally the nitrite and chloride) salts of calcium, iron, and magnesium. (b) Commonly computed from the amount of calcium and magnesium in the water and expressed as equivalent calcium carbonate.

**HARDNESS, CARBONATE** - Hardness caused by the presence of carbonates and bicarbonates of calcium and magnesium in water. Such hardness may be removed to the limit of solubility by boiling the water. This is also called temporary hardness.

**HARDNESS, NONCARBONATE** - Hardness caused by calcium and magnesium sulfates and chlorides and compounds other than carbonates which cannot be reduced materially by boiling the water. (Also called "permanent hardness.")

**HARDNESS, TOTAL** - The sum of carbonate and noncarbonate hardness.

**HYDROGEN ION CONCENTRATION** - Commonly expressed as the pH value that represents the logarithm of the reciprocal of the hydrogen ion concentration.

**INHIBITOR (APPLIED TO CORROSION)** - A chemical substance or mixture which effectively decreases corrosion when added to a liquid (usually in small concentrations).

**ION** - A particle, atom, or group of atoms carrying either a positive or negative electrical charge which is formed when an electrolyte is dissolved in water.

**ION EXCHANGE** - A process where water is passed through a granular material and ions on the granular material are replaced by ions contained in the water. For example, in the zeolite softening process the sodium ions ( $\text{Na}^+$ ) of the granular zeolite are replaced by the calcium ions ( $\text{Ca}^{++}$ ) in the water to leave the water free of calcium (the cause of hardness) but with an increased amount of sodium.

**LANGELIER SATURATION INDEX (LSI)** - A calculated value used to predict only the calcium carbonate scaling tendency of water. A positive number indicates scale forming tendencies; a negative number indicates no scale will form. (LSI calculation included in Table 6.)

**MAKEUP WATER** - Water supplied to replace the loss in a system by leaks, evaporation, wind drifts, bleedoff, blowdown, or withdrawal.

**MICROBIOCIDES** - Material used to destroy microorganisms.

**MICROMHO** - An electrical unit of conductance (one millionth of a mho) which is the reciprocal of electrical resistance.

**MICROORGANISM** - A minute plant or animal in water or earth that is visible only through a microscope.

**MILLIGRAMS PER LITER (mg/l)** - A unit of the concentration of water or wastewater constituent. It is 0.001 gram of the constituent in 1,000 milliliters of water.

NEUTRALIZING AMINES - Chemicals used to neutralize carbon dioxide in steam condensate to prevent corrosion.

NORMALITY - The concentration of a solution in relation to a normal solution. The normal solution contains a specific weight of a substance per liter, based on the characteristics of the substance. Thus, a half-normal solution would be expressed as 0.5 N or N/2.

OPEN RECIRCULATING WATER SYSTEM - A water circulating system that is open to the atmosphere and cooling is accomplished by evaporation.

OXYGEN SCAVENGER - A chemical used to remove final traces of oxygen from a boiler feedwater.

pH - Measure of hydrogen ion concentration indicating degrees of acidity or alkalinity of a solution. The range pH varies from 1 to 14. Values below 7.0 indicate acidity and above 7.0 alkalinity.

pH SATURATION VALUE ( $\text{pH}_s$ ) - The pH produced when carbon dioxide is added or removed from the solution bringing the water into equilibrium with solid calcium carbonate. ( $\text{pH}_s$  calculation included in Table 6.)

PHOSPHATES - Chemicals used for corrosion control in cooling towers and for deposit control in boilers. Commonly these occur as orthophosphates or polyphosphates. The level of the active phosphate chemical is reported either as percent  $\text{P}_2\text{O}_5$  (phosphorus pentoxide) or as  $\text{PO}_4$  (phosphate) with these related by factor as follows:  $\text{PO}_4 = 1.34 \times \text{P}_2\text{O}_5$ .

PRECIPITATE - (a) To separate a substance in solid form from a solution. (b) The substance in solid form which has been separated from a solution.

RAW WATER - Water used as a source of water supply taken from a natural or impounded body of water such as a stream, lake, or ground water aquifer.

REGENERATION - That part of the operating cycle of an ion exchange process in which a specific chemical solution is passed through the ion exchange bed to prepare it for a service run.

RYZNAR STABILITY INDEX (RSI) - A modification of the LSI that indicates the water tendency to form scale. Values below 6.0 indicate the water has calcium carbonate scale forming tendencies; values above 6.0 indicate no scale will form. (RSI calculation included in Table 6.)

SATURATION - The condition of a liquid when it has taken into solution the maximum quantity of any substance at a given temperature and pressure.

**SCALE** - Deposition on a heat transfer surface of normally soluble salts. Scale is usually crystalline and dense, frequently laminated, and occasionally columnar in structure.

**SILT** - Suspended insoluble material such as dust, dirt, or pollen in water.

**SLIME** - Biological growths that may accumulate to the extent they foul equipment.

**SLUDGE** - A water-formed deposit that will settle and may include all suspended solids carried by water. Sludge is commonly formed in boilers, where it may be baked into place and become hard and adherent.

**SOFTENING WATER** - The process of removing from water certain mineral substances which produce a condition called hardness. There are two softening processes in general use: Chemical precipitation (lime-soda softening) and the zeolite ion exchange process.

**SOLIDS, SUSPENDED** - All matter in water which is not dissolved and which can be removed with filtration.

**SOLIDS, DISSOLVED** - The total concentration of all substances in a filtered solution which exist as solids after the liquid is completely evaporated from the solution.

**SOLIDS, TOTAL** - The sum of the suspended and dissolved matter (solids).

**TUBERCULATION** - Knoblike mounds or growths that are often the result of corrosion. Also called tubercles.

**TURBIDITY** - A condition in water caused by the presence of suspended matter resulting in the scattering and absorption of light rays. A measure of fine suspended matter in liquids.

**VOLATILE** - Passing off readily in the form of vapor.



**APPENDIX B**

**WATER SAMPLE TEST PROCEDURES**

## WATER SAMPLE TEST PROCEDURES

**Purpose of Testing.** Testing of industrial water is done to determine the amount of treatment chemicals in the water so that dosage levels can be properly regulated. These tests are the only known means of having reliable operations, as far as the water is concerned.

**Field Laboratory Test Procedures.** The test procedures in this appendix are basically for use in a permanent field laboratory. The former Air Force Industrial Water Treatment contractor has agreed to provide the "apparatus" and "reagents" numbers in parentheses. These items can be obtained by sending a direct purchase request to ASCI, 112 East 2nd St, Duluth, MN 55805 (218) 722-4040.

**Portable Test Kits.** Portable test kits listed below are primarily for use in the permanent field laboratory but may also be used at the site location where the sample is taken.

Item No	<u>Test Kit</u>
3100	Lignosulfonate, Hach Kit TA-3, or equal. Measures sodium lignosulfonate, as ppm tannic acid.
3200	Molybdate, Taylor Kit, K-1805, or equal. Measures Molybdate, as ppm $\text{MoO}_4$ .
3300	Silica, Hach Kit SI-5, or equal. Measures silica, as ppm $\text{SiO}_2$ .
3400	Iron, Hach Kit IR-18, or equal. Measures iron, as ppm Fe
3500	Phosphonate, Taylor K-1583 (CR), or equal Measures phosphonate, as ppm Dequest 2000. (1 drop = 2 ppm).

**Testing Techniques.** Accurate test results depend on following good basic laboratory procedures and techniques.

a. Water analyses require certain chemical apparatus. These are scientific instruments and are to be treated as such. The apparatus should be HANDLED WITH CARE!

b. It is necessary to keep everything in GOOD ORDER at all times. Have a place for everything, and everything in its place! Be sure all bottles are properly labeled and avoid mixing bottles!! All bottles should be tightly closed. Keep any reserve stock of solutions and reagents in a cool, dark place.

c. All equipment and apparatus should be kept CLEAN! Unless this is done, the tests will not be reliable and errors will be introduced. Thoroughly rinse and dry all glassware immediately after use. If color apparatus are employed, do not expose to heat or to direct sunlight. If any liquid is spilled on any of the equipment or apparatus, wipe off at once and dry.

d. MEASURE CAREFULLY! The apparatus are precision instruments that are capable of very fine measurements. The results will be "off" if improper amounts of samples are taken, if incorrect volumes of solution are added, if the burette is not read correctly, or if the methods prescribed on the following pages are not performed exactly as written.

e. The SUSPENDED MATTER OR SLUDGE will generally settle to the bottom if the sample is allowed to stand before testing. The clear water can then be used for the tests, making it unnecessary to filter (except for specific tests). Theoretically, all water analyses should be made at 77 °F (25 °C); however, no appreciable error will be introduced if the test is made between 68 and 86 °F (20 to 30 °C). In general, the shorter the time between the collection and the analysis of the sample, the more reliable will be the results.

f. When the water sample color interferes with the analysis, it may be necessary to filter the sample through activated charcoal, except for the sulfite and nitrite tests.



TABLE B-1. PHENOLPHTHALEIN (P) ALKALINITY

TEST PROCEDURES

APPARATUS:

Burette, 10 ml, Automatic (for N/50 Sulfuric Acid) (item 1001)  
 Graduated Cylinder, 50 ml, Plastic (item 1004)  
 Bottle, w/Dropper (for Phenolphthalein Indicator) 2 oz (item 1005)  
 Casserole, Porcelain, Heavy Duty, 200 ml Capacity (item 1003)  
 Stirring Rod, Plastic (item 1006)

REAGENTS:

Standard Sulfuric Acid Solution, N/50 (item 2001)  
 Phenolphthalein Indicator Solution, 1 percent (item 2040)

METHOD:

1. Measure the amount of water to be tested in the graduated cylinder. The amount should be based on the expected results of the test according to the following:

P Alkalinity Expected, as $\text{CaCO}_3$	Sample Size	Factor
Less than 100 ppm	50 ml	20
More than 100 ppm	20 ml	50

2. Pour into the casserole.

3. Add 6 drops of Phenolphthalein Indicator Solution to the casserole and stir. If the water does not change to a red color, there is no phenolphthalein alkalinity present and the "P" reading is reported as "zero." If the water does change to red color, "P" alkalinity is present and the test should be continued.

4. Squeeze the rubber bulb to force the Standard Sulfuric Acid Solution from the bottle to fill the burette just above the zero mark; then allow the excess to drain back automatically into the bottle.

5. While stirring the water constantly, add Standard Sulfuric Acid slowly from the burette to the casserole until the red color disappears and the water resumes the original color of the sample before the Phenolphthalein Indicator Solution was added. This is the end point. Read the burette to the nearest 0.1 ml.

RESULTS:

The P alkalinity (ppm as  $\text{CaCO}_3$ ) is calculated as follows:

$$\text{P alkalinity (ppm as } \text{CaCO}_3) = (\text{ml acid}) \times (\text{factor})$$

EXAMPLE:

4.3 ml of N/50 sulfuric acid were required to change the color of a 50 ml sample of water from red to colorless:

$$\text{P alkalinity} = 4.3 \times 20 = 86 \text{ ppm as } \text{CaCO}_3$$

## TABLE B-2. TOTAL (M) ALKALINITY

### TEST PROCEDURES

#### APPARATUS:

Burette, 10 ml, Automatic (for N/50 Sulfuric Acid) (item 1001)  
Graduated Cylinder, 50 ml, Plastic (item 1004)  
Bottle, w/Dropper (for Mixed Indicator), 2 oz (item 1005)  
Casserole, Porcelain, Heavy Duty, 200 ml Capacity (item 1003)  
Stirring Rod, Plastic (item 1006)

#### REAGENTS:

Standard Sulfuric Acid Solution, N/50 (item 2001)  
Mixed Indicator Solution (item 2036)

#### METHOD:

1. Measure the amount of water to be tested in the graduated cylinder. The amount should be based on the expected results of the tests according to the following:

M Alkalinity Expected as $\text{CaCO}_3$	Sample Size	Factor
Less than 100 ppm	50 ml	20
More than 100 ppm	20 ml	50

2. Pour into the casserole.

3. Add 10 drops of Mixed Indicator Solution to the casserole and stir.

4. If the water changes to a light pink color, free mineral acid is present. There is no mixed indicator alkalinity, and the "M" reading is reported as "zero."

5. If the water changes to a green or blue color, "M" alkalinity is present and the test should be continued.

6. Squeeze the rubber bulb to force the Standard Sulfuric Acid Solution to fill the burette to just above the zero mark; then allow the excess solution to drain back automatically into the bottle.

7. While stirring the water constantly, add Standard Sulfuric Acid Solution slowly from the burette to the casserole until the green or blue color changes to light pink. This is the end point. Read the burette to the nearest 0.1 ml.

RESULTS:

The M alkalinity (ppm as  $\text{CaCO}_3$ ) is calculated as follows:

$$\text{M alkalinity (ppm as } \text{CaCO}_3) = (\text{ml acid}) \times (\text{factor})$$

EXAMPLE:

5.9 ml of N/50 sulfuric acid were required to change the color of a 50 ml sample of water from green to light pink.

$$\text{M alkalinity} = 5.9 \times 20 = 118 \text{ ppm as } \text{CaCO}_3.$$

NOTES:

1. If the end point color is difficult to see, repeat the entire test using 15 drops of Mixed Indicator Solution.
2. Just before the end point is reached, the green or blue color fades to a light blue color and then becomes light pink. The end point is the first appearance of a permanent pink color.

TABLE B-3. HYDROXYL (OH) ALKALINITY (CAUSTICITY)

TEST PROCEDURES

APPARATUS:

Burette, 10 ml Automatic (for N/50 Sulfuric Acid Solution)  
(item 1001)  
Graduated Cylinder, 50 ml, Plastic (item 1004)  
Bottle, w/Dropper (for Phenolphthalein Indicator Solution), 2  
oz (item 1005)  
Casserole, Porcelain, Heavy Duty, 200 ml Capacity (item 1003)  
Stirring Rod, Plastic (item 1006)  
Graduated Cylinder, 10 ml, Plastic (item 1033)

REAGENTS:

Standard Sulfuric Acid Solution, N/50 (item 2001)  
Barium Chloride Reagent Solution, 10 percent (item 2035)  
Phenolphthalein Indicator Solution, 1 percent (item 2040)

METHOD:

1. Measure the amount of the water to be tested in the graduated cylinder. The amount should be based on the expected results of the tests according to the following:  

OH Alkalinity Expected, as $\text{CaCO}_3$	Single Size	Factor
Less than 100 ppm	50 ml	20
More than 100 ppm	20 ml	50
2. Pour into the casserole.
3. Add 5 ml of Barium Chloride Solution to the casserole.
4. Stir the water vigorously for 30 to 60 seconds.
5. Add 10 drops of Phenolphthalein Indicator Solution to the casserole. If the water does not change to a red color, there is no hydroxyl alkalinity present and the "OH" reading is reported as "zero." If the water does change to a red color, hydroxyl alkalinity is present and the test should be continued.
6. Squeeze the rubber bulb to force the Standard Sulfuric Acid Solution to fill the burette to just above the zero mark; then allow the excess to drain back automatically into the bottle.
7. While stirring the water constantly, add Standard Sulfuric Acid Solution slowly from the burette to the casserole until the red color disappears and the water turns white or a whitish gray. This is the end point. Read the burette to the nearest 0.1 ml.

**RESULTS:**

The OH alkalinity (ppm as  $\text{CaCO}_3$ ) is calculated as follows:

$$\text{OH alkalinity (ppm as } \text{CaCO}_3) = (\text{ml acid}) \times (\text{factor})$$

**EXAMPLE:**

4.4 ml of N/50 sulfuric acid were required to change the color of a 20 ml sample of water from red to white or whitish gray.

$$\text{OH alkalinity} = 4.4 \times 50 = 220 \text{ ppm as } \text{CaCO}_3$$

## TABLE B-4. CONDUCTIVITY

### TEST PROCEDURES

#### APPARATUS:

1. Conductivity Meter, Complete (item 1014 or item 1034)  
(Authorized by TA 404 - This item is available through normal supply channels. It is not furnished by the check-analysis laboratory.)
2. In general, there are two types of conductivity meters. One has an electrode that is put into a cell containing the water to be tested. The other has a small cup mounted on the meter into which the water to be tested is poured. Either type of meter may be automatically temperature compensated, or the meter may require a temperature correction. The meter may indicate TDS or conductivity as micromhos, but either measurement represents the same characteristic of the water sample. Where the meter is designed to give either measurement, it is important to always use the same measurement to avoid an error.

Cylinder, Ungraduated, Footed Base, about 5 inches high x 1 1/2-inch diameter (item 1016)

Thermometer, Dial Type (item 1013)

#### REAGENTS:

Phenolphthalein Indicator, 1 percent (item 2040)

Gallic Acid Powder (item 2063)

#### METHOD:

It is necessary to follow the instructions furnished with the conductivity meter that is being used. The general procedure should be similar to the following steps.

1. The quantity of water sample should be as specified for the meter.
2. Add 3 drops of Phenolphthalein Indicator. If the sample turns red, add Gallic Acid Powder until the red color disappears. If the water does not turn red when the Phenolphthalein Indicator is added, continue the test.
3. Follow the instructions for the meter to measure the conductivity, using the appropriate method (that is, with or without the acid addition).

## RESULTS:

Depending upon the type of meter used, the results are read as either conductivity in micromhos or TDS in ppm. The relationship between these measurements when these procedures are used is as follows:

$$\begin{aligned}\text{TDS, ppm} &= 0.66 \times \text{Conductivity, micromhos} \\ \text{Conductivity, micromhos} &= 1.5 \times \text{TDS, ppm}.\end{aligned}$$

## NOTES:

1. Periodically the meter should be calibrated against a standard solution.
2. Two standard potassium chloride solutions are available from the check-analysis laboratory:
  - a. Item 2095 - 500 micromhos
  - b. Item 2096 - 7,000 micromhos

## TABLE B-5. pH-ELECTROMETRIC METHOD

### TEST PROCEDURES

#### APPARATUS:

pH Meter, Complete (item 1015 or item 1035)  
(Authorized by TA 404 - This item is available through normal supply channels.)  
Beaker, 150 ml, Heavy Duty Plastic (3 each) (item 1012)  
Wash Bottle, 500 ml, Heavy Duty Plastic (item 1011)

#### REAGENTS:

Standard pH Buffer Solution, pH-4 (item 2074)  
Standard pH Buffer Solution, pH-7 (item 2075)  
Standard pH Buffer Solution, pH-10 (item 2076)

#### METHOD:

Carefully follow the procedures provided with the pH meter. They should be similar to the following:

1. Turn the meter from "standby" to "on" position.
2. Standardize instrument by immersing the electrode(s) in two different Standard pH Buffer Solutions in the test beaker as follows:
  - a. Place electrode(s) in pH-7 Buffer Solution and adjust the meter to read pH-7.
  - b. Place electrode(s) in the second pH Buffer Solution, either the pH-4 or pH-10, depending on the suspected range of the unknown sample to be tested, and adjust the meter to the same pH.
3. Remove electrode(s) and thoroughly wash with distilled or condensate water.
4. Immerse the electrode(s) in the water sample and turn the meter to "test" or "pH" position and read meter.
5. Rinse the electrodes with distilled or condensate water and turn the instrument to the "standby" position. Do not turn off.

#### NOTES:

1. When not in use, keep the glass electrode soaking in a pH-4 Buffer Solution.
2. When not in use, keep the plastic cap on the reference electrode. Some reference electrodes must be kept full of electrolyte. Follow the instrument instructions on this.



## TABLE B-6. pH-COLORIMETRIC METHOD

### TEST PROCEDURE

#### APPARATUS:

Comparator Slide Base, Taylor No. 9190, or equal (item 1017)  
Test Tube, 5 ml, Taylor No. 4023, or equal (item 1018)  
Pipette, 0.5 ml Capacity, Taylor No. 4028, or equal (item 1019)  
Test Tube Brush, for 5 ml Test Tube, Taylor No. 6002, or equal (item 1020)  
pH Slide, range 5.2 to 6.8, Taylor No. 9065, or equal (item 1021)  
pH Slide, range 6.0 to 7.6, Taylor No. 9066, or equal (item 1022)  
pH Slide, range 6.8 to 8.4, Taylor No. 9067, or equal (item 1023)  
pH Slide, range 7.6 to 9.2, Taylor No. 9069, or equal (item 1024)  
pH Slide, range 8.0 to 11.2, Taylor No. 9077, or equal (item 1025)  
pH Slide, range 11.0 to 12.6, Taylor No. 9074, or equal (item 1036)  
Dalite Lamp, 120v, 60 Hz, Taylor No. 9195, or equal (item 1026)

#### REAGENTS:

Chlorphenol Red Indicator (5.2 to 6.8 pH), Taylor No. R-1003G, or equal (item 2084)  
Bromthymol Blue Indicator (6.0 to 7.6 pH), Taylor No. R-1003H, or equal (item 2085)  
Phenol Red Indicator (6.8 to 8.4 pH), Taylor No. R-1003J, or equal (item 2086)  
Meta Cresol Purple Indicator (7.6 to 9.2 pH), Taylor No. R-1003L, or equal (item 2087)  
Thymol Red Indicator (8.0 to 11.2 pH), Taylor No. R-1003T, or equal (item 2088)  
Parazo Orange Indicator (11.0 to 12.6 pH), Taylor No. R-1003Q, or equal (item 2089)

#### PREPARATION OF SAMPLE:

The sample should be taken at room temperature, through a cooling coil if necessary, and in such a manner as to prevent contamination and contact with the air. The test should be made immediately after taking the sample, and the sample should not be filtered. The container in which the sample is taken and all three 5 ml test tubes used in the test should be rinsed repeatedly with the sample before making the determination.

#### METHOD:

1. Fill three 5 ml test tubes exactly to the mark with the sample.
2. Place in the three center holes in the base of the comparator.
3. By means of the pipette, add 0.5 ml of the appropriate indicator to the middle tube only, and stopper the tube.
4. Remove the middle tube from the base, mix the sample and the indicator by inverting the tube, and replace the tube in the middle hole.
5. Place the comparator base on the shelf of the Dalite lamp. Turn switch ON.
6. Place the pH color slide corresponding to the indicator used on the comparator base.
7. Move the pH color standard slide to the right or left until the intensity of the color of the sample is matched by one of the color standards of the slide.

#### RESULTS:

The pH value is the number appearing on the slide, as indicated by the arrow on the base.

#### NOTES:

1. If the sample does not match one of the color standards of the slide, (a) the sample may not be in the pH range of the slide and the test should be repeated using a different indicator and the corresponding pH color standard slide, or (b) the sample may have become contaminated in handling, or (c) the indicator solution may have deteriorated or become contaminated by acid or alkali fumes, dust, etc. In case of contamination, repeat the test with a fresh sample and, if necessary, employ fresh indicator solution.
2. If the pH indicated is at the extreme low end of the pH range of an indicator, as for example, pH 6.8 when using Phenol Red, repeat the test using the lower range indicator, as Bromthymol Blue. If the pH indicated is at the high end of the indicator range, as pH 7.6 with the Bromthymol Blue, repeat the test using the higher range indicator, Phenol Red.
3. Samples with high levels of lignosulfonates will interfere with the color obtained.

## TABLE B-7. TOTAL HARDNESS

### TEST PROCEDURES

#### APPARATUS:

Burette, 10 ml Automatic (for Hardness Titrating Solution) (item 1001)  
Graduated Cylinder, 50 ml, Plastic (item 1004)  
Casserole, Porcelain, Heavy Duty, 200 ml Capacity (item 1003)  
Stirring Rod, Plastic (item 1006)  
Spoon, Plastic, 0.1 gm Capacity (item 1007)  
Bottle, w/Dropper, 2 oz (for Hardness Buffer Solution) (item 1005)

#### REAGENTS:

Standard Hardness Titrating Solution, 1 ml = 1 mg  $\text{CaCO}_3$  (item 2029)  
Hardness Buffer Solution (item 2065)  
Hardness Indicator Powder (item 2056)

#### METHOD:

1. Measure the amount of water to be tested in the graduated cylinder. The amount should be based on the expected results of the test according to the following:

Hardness Expected, as $\text{CaCO}_3$	Sample Size	Factor
Less than 100 ppm	50 ml	20
More than 100 ppm	20 ml	50

2. Pour the sample into the casserole.

3. Add 1 ml Hardness Buffer Solution and 1 spoon of Hardness Indicator Powder to the sample. If the water turns blue, there is no hardness present, and it is reported as zero. If the water turns purple or red, then the test should be continued.

4. Squeeze the rubber bulb to force the Standard Hardness Titrating Solution from the bottle to fill the burette just above the zero mark; then allow the excess to drain back automatically into the bottle.

5. While stirring the sample constantly, add Standard Hardness Titrating solution slowly from the burette to the casserole until the purple or red color changes to blue. This is the end point. Read the burette to the nearest 0.1 ml.

## RESULTS:

The total hardness (TH), ppm as  $\text{CaCO}_3$ , is obtained as follows:  
Total hardness, ppm = (ml solution) x (factor).

## EXAMPLE:

6.5 ml of the Standard Hardness Titrating Solution were required to change the color of a 50 ml sample of water from red or purple to blue.

$$\text{Total hardness} = 6.5 \times 20 = 130 \text{ ppm as } \text{CaCO}_3$$

NOTE: When testing water softener effluent, use a 200 ml sample and a factor of 5, or a 500 ml sample and a factor of 2.

## TABLE B-8. CALCIUM HARDNESS

### TEST PROCEDURES

#### APPARATUS:

Burette (2 each), 10 ml, Automatic (for Hardness Titrating Solution and Sulfuric Acid Solution) (item 1001)  
Graduated Cylinder, 50 ml, Plastic (item 1004)  
Bottle, w/Dropper, 2 oz (2 each) (for Mixed Indicator and Sodium Hydroxide) (item 1005)  
Casserole, Porcelain, Heavy Duty, 200 ml Capacity (item 1003)  
Stirring Rod, Plastic (item 1006)  
Plastic Measuring Cup, 0.1 gm Capacity (item 1007)

#### REAGENTS:

Standard Sulfuric Acid, N/50 (item 2001)  
Mixed Indicator Solution (item 2036)  
Standard Hardness Titrating Solution, 1 ml = 1 mg  $\text{CaCO}_3$  (item 2029)  
Sodium Hydroxide Solution, 1.0 N (item 2008)-CAUTION STRONG CAUSTIC.  
Calcium Indicator Powder (item 2053)

#### METHOD:

1. Measure the amount of water to be tested in a graduated cylinder. The amount should be based on the expected results of the test according to the following:

Ca Hardness Expected, as $\text{CaCO}_3$		
	Sample Size	Factor
Less than 400 ppm	50 ml	20
More than 400 ppm	20 ml	50

2. Pour the sample into the casserole.

3. Add 3 drops of Mixed Indicator Solution. If the sample turns light pink, go to step 5. If the sample turns green, continue the test with step 4.

4. Add the standard Sulfuric Acid to the casserole with constant stirring until the sample turns light pink. There is no need to measure the amount of acid added, since this does not affect the calculation of test results.

5. Add 2 measuring cups of Calcium Indicator Powder and 2 ml of the Sodium Hydroxide Solution to the casserole.

6. Squeeze the rubber bulb to force the Standard Hardness Titrating Solution from the bottle to fill the burette just above the zero mark; then allow the excess to drain back automatically into the bottle.

7. While stirring the sample constantly, add Standard Hardness Titrating Solution slowly from the burette to the casserole until the color changes to deep purple. This is the end point. (The sample, which is a pink color, will develop a purple tinge as the end point is approached.) Read the burette to the nearest 0.1 ml.

#### RESULTS:

The Calcium hardness (Ca H), ppm as  $\text{CaCO}_3$ , is obtained as follows:

$$\text{Calcium hardness, ppm as } \text{CaCO}_3 = (\text{ml solution}) \times (\text{factor}).$$

#### EXAMPLE:

4.9 ml of Standard Hardness Titrating Solution were required to change the color of a 50 ml sample of water from light pink to a deep purple.

$$\text{Calcium hardness} = 4.9 \times 20 = 98 \text{ ppm as } \text{CaCO}_3$$

TABLE B-9. MAGNESIUM HARDNESS

TEST PROCEDURES

METHOD:

The Magnesium hardness (Mg H), ppm as  $\text{CaCO}_3$ , is calculated as the difference between the total hardness and the calcium hardness.

EXAMPLE:

The Total hardness of a water is 130 ppm and the calcium hardness is 98 ppm. The magnesium hardness is:

$$\text{Magnesium hardness} = 130 - 98 = 32 \text{ ppm as } \text{CaCO}_3$$

## TABLE B-10. ORTHOPHOSPHATE

### TEST PROCEDURES

#### APPARATUS:

Comparator Slide Base, Taylor No. 9190, or equal (item 1017)  
High Phosphate Comparator, Range 5 to 100 ppm, Taylor No. 9180, or equal (item 1028)  
Phosphate Mixing Tube, Graduated at 5, 15, and 17.5 ml, with Rubber Stopper, Taylor No. 4021, or equal (items 1029 and 1030)  
Test Tube, 5 ml (two required) (item 1018)  
Wash Bottle for Molybdate Reagent (item 1011)  
Funnel, Plastic (item 1009)  
Filter Paper, Whatman No. 5, 12.5 cm dia, or equal (item 1010)  
Dalite Lamp, Taylor No. 9195, or equal, 120 V, 60 Hz (item 1026)  
Test Tube Cleaning Brush (item 1020)  
Measuring Cup, Plastic, 0.1 gm Capacity (item 1007)  
Beaker, Plastic, 150 ml Capacity (two required) (item 1012)

#### REAGENTS:

Phosphate Indicator Powder (item 2050)  
Molybdate Reagent Solution (item 2032) - CAUTION STRONG ACID.  
Distilled Water

#### PREPARATION OF WATER SAMPLE TO BE TESTED:

It is imperative the water sample to be tested be free from suspended matter or sludge. Mere traces will cause serious errors. Filter the water into the beaker and through the same filter paper as many times as required to produce a clear sample.

#### METHOD:

1. Fill the phosphate mixing tube to the 5 ml (bottom) mark with the filtered water sample.
2. Fill to the 15 ml (middle) mark with Molybdate Reagent Solution.
3. Add 2 LEVEL measuring dipperfuls of the Phosphate Indicator Powder to the phosphate mixing tube.
4. Insert the rubber stopper and mix. If a blue color does not develop in 3 minutes, there are no phosphates present; the  $\text{PO}_4$  reading is reported as "zero;" and the test discontinued. If phosphates are present, a blue color will develop and the test should be continued.



5. Place the phosphate mixing tube in the middle hole of the comparator.
6. Fill two 5 ml test tubes with filtered water samples and place the test tubes in the holes on either side of the phosphate mixing tube.
7. Place comparator on shelf of the Dalite lamp. Turn switch ON.
8. Move the color standard slide to the right or left until the intensity of the color of the sample is matched by one of the color standards of the slide.

#### RESULTS:

The phosphate, in ppm  $\text{PO}_4$ , is the number appearing on the slide as indicated by the arrow on the base. If the phosphate exceeds 80 ppm, discard the test. Repeat the test, using 2.5 ml of the filtered water sample (instead of 5 ml); dilute to the (bottom) mark (5 ml) with distilled water or condensate water and repeat the test starting with step 2. Multiply reading by 2 to obtain  $\text{PO}_4$  in ppm.

## TABLE B-11. TOTAL PHOSPHATE

### TEST PROCEDURES

#### APPARATUS:

Comparator Slide Base, Taylor No. 9190, or equal (item 1017)  
High Phosphate Comparator, Range 5 to 100 ppm, Taylor No. 9119, or equal (item 1028)  
Phosphate Mixing Tube Graduated at 5, 15, and 17 5 ml with Rubber Stopper, Taylor No. 4021, or equal (items 1029 and 1030)  
Test Tube, 5 ml (two required), Taylor No. 4023, or equal (item 1018)  
Wash Bottle for Molybdate Reagent (item 1011)  
Funnel, Plastic (item 1009)  
Filter Paper, Whatman No. 5, 12 5 cm. dia, or equal (item 1026)  
Test Tube Cleaning Brush (item 1020)  
Measuring Cup, Plastic 0.1 gm Capacity (item 1007)  
Beaker, Plastic, 150 ml Capacity (item 1012)  
Erlenmeyer Flask, 250 ml, Glass (item 1031)  
Hot Plate, 120 V, 60 Hz (item 1032)  
Graduated Cylinder, 50 ml, Plastic (item 1004)

#### REAGENTS:

Sulfuric Acid Solution, 4 N (item 2005) - CAUTION STRONG ACID  
Sodium Hydroxide Solution, 4 N (item 2012) - CAUTION STRONG CAUSTIC.  
Phosphate Indicator Powder (item 2050)  
Molybdate Reagent Solution (item 2032) - CAUTION STRONG ACID  
Distilled Water.

#### PREPARATION FOR WATER SAMPLE TO BE TESTED:

It is imperative that the water sample to be tested be free from suspended matter. Mere traces will cause serious errors. Filter the water into the beaker and through the same filter paper as many times as required to produce a clear sample.

#### METHOD:

1. Measure 25 ml of the filtered water sample in the 50 ml graduate cylinder.
2. Pour into the Erlenmeyer flask.
3. Measure 5 ml of 4 N Sulfuric Acid (reversion acid) in the 10 ml cylinder and slowly pour into the Erlenmeyer flask.

4. Heat the flask just to boiling (electric hot plate) and then turn the heat down so that the water simmers for 15 to 20 minutes. The heating should be done gently so that not more than half of the mixture evaporates. A clean funnel placed in the mouth of the flask will reduce evaporation. In no case should the rate of heating cause white fumes to be given off. If this happens, discard the sample and start the test over.
5. Cool the mixture to room temperature.
6. Add 5 ml of 4 N Sodium Hydroxide (reversion neutralizer).
7. Pour the contents of the flask into the graduated cylinder.
8. Add distilled water to the graduated cylinder to fill to the 25 ml mark, then mix the contents of the graduate.
9. Fill the phosphate mixing tube to the 5 ml (bottom) mark with the prepared water sample from the graduated cylinder.
10. Fill to the 15 ml (middle) mark with Molybdate Reagent Solution.
11. Add 2 LEVEL measuring dipperfuls of the Phosphate Indicator Powder to the phosphate mixing tube.
12. Insert the rubber stopper and mix. If a blue color does not develop in 3 minutes, there are no phosphates present; the total  $\text{PO}_4$  reading is reported as "zero" and the test is discontinued. If phosphates are present, a blue color will develop and the test is continued.
13. Place the phosphate mixing tube in the middle hole of the comparator.
14. Fill two 5 ml test tubes with filtered water samples and place the test tubes in the holes on either side of the phosphate mixing tube.
15. Place the comparator on the shelf of the Dalite lamp. Turn switch ON.
16. Move the color standard slide to the right or left until the intensity of the color of the sample is matched by one of the color standards of the slide.

#### RESULTS:

The phosphate, in ppm  $\text{PO}_4$ , is the number appearing on the slide as indicated by the arrow on the base. If the phosphate exceeds 80 ppm, discard the test. Repeat the test, using 2.5 ml of the filtered water sample (instead of 5 ml); dilute with distilled or condensate water and repeat the test starting with step 10. Multiply reading by 2 to obtain  $\text{PO}_4$  in ppm.

## TABLE B-12. SULFITE

### TEST PROCEDURES

#### APPARATUS:

Burette, 10 ml, Automatic (for Potassium Iodide-Iodate Solution) (item 1001)  
Graduated Cylinder, 50 ml, Plastic (item 1004)  
Bottle, w/Dropper (for Phenolphthalein Indicator Solution), 2 oz (item 1005)  
Casserole, Porcelain, Heavy Duty, 200 ml Capacity (item 1003)  
Measuring Scoop, Plastic, 1 gm Capacity (item 1008)  
Stirring Rod, Plastic (item 1006)

#### REAGENTS:

Standard Potassium Iodide-Iodate Solution, 0.0125 N (item 2017)  
Phenolphthalein Indicator Solution, 1 percent (item 2040)  
Dual Purpose Sulfite Indicator Powder (item 2060) - CAUTION STRONG ACID

#### METHOD:

1. Measure the amount of water to be tested in the graduated cylinder. The amount should be based on the expected results of the test according to the following:

Sulfite Expected, as $\text{SO}_3$	Sample Size	Factor
Less than 100 ppm	50 ml	10
100 to 500 ppm	10 ml	50

2. Pour into the casserole.

3. Add 5 drops of Phenolphthalein Indicator Solution to the casserole.

4. Add 2 or more "scoopfuls" of Sulfite Indicator Powder to the sample in the casserole and stir slowly until the red color disappears.

5. Squeeze the rubber bulb to force the Standard Potassium Iodide-Iodate Solution to fill the burette to just above the zero mark; then allow the excess to drain back automatically into the bottle.

6. While stirring the sample constantly add Potassium Iodide-Iodate solution slowly from the burette to the casserole until a faint but permanent blue color appears. This is the end point. Read the burette to the nearest 0.1 ml.

## RESULTS:

The sulfite level, in ppm  $\text{SO}_3$ , is calculated as follows:

Sulfite, ppm = (ml solution) x (factor).

## EXAMPLE:

2.3 ml of Potassium Iodide - Iodate Solution were required to change the color of a 50 ml sample of the water from colorless to faint blue.

Sulfite =  $2.3 \times 10 = 23$  ppm  $\text{SO}_3$

## NOTES:

1. To ensure accurate results, water samples should be cooled with minimum exposure to air.
2. The test should be done as quickly as possible to reduce the introduction of oxygen.
3. Use a minimum of 2 scoopfuls of Sulfite Indicator Powder plus any additional amount to neutralize all the alkalinity (elimination of red color) in the water to be tested, as indicated in step 4 of the method.
4. The end point is the first appearance of a faint, permanent blue color and not the deep blue color that develops if Potassium Iodide-Iodate is added past the end point.
5. To express sulfite levels as ppm sodium sulfite ( $\text{Na}_2\text{SO}_3$ ), multiply ppm  $\text{SO}_3$  by 1.575. EXAMPLE: 23 ppm  $\text{SO}_3$  is equal to 1.575 X 23 or 36 ppm as  $\text{Na}_2\text{SO}_3$ .

## TABLE B-13. NITRITE

### TEST PROCEDURES

#### APPARATUS:

Burette, 10 ml, Automatic (for Ceric Sulfate Solution) (item 1001)  
Graduated Cylinder, 50 ml, Plastic (item 1004)  
Bottle, w/Dropper, (for Nitrite Indicator Solution), 2 oz (item 1005)  
Casserole, Porcelain, Heavy Duty, 200 ml Capacity (item 1003)  
Stirring Rod, Plastic (item 1006)

#### REAGENTS:

Standard Ceric Sulfate Titrating Solution, 0.11 N (item 2020)  
Nitrite Indicator Solution (item 2042) - CAUTION STRONG ACID

#### METHOD:

1. Measure 25 ml of the water to be tested in the cylinder.
2. Pour the water into casserole.
3. Add 2 drops of Nitrite Indicator Solution. If the water turns blue or blue green, no nitrite is present, and the nitrite reading is reported as zero. If the water turns red, nitrite is present and the test is continued.
4. Squeeze the rubber bulb of the automatic burette to force the Ceric Sulfate Solution from the bottle to fill the burette to just above the zero mark; then allow the excess to drain back automatically into the bottle.
5. Add Ceric Sulfate Solution from the burette to the casserole, drop by drop, until the color changes from red to light blue or blue green for 30 seconds. This is the end point. Read the burette to the nearest 0.1 ml.

#### RESULTS:

The nitrite, in ppm  $\text{NO}_2$ , is calculated as follows:

$$\text{Nitrite, ppm NO}_2 = (\text{ml solution}) \times 100$$

#### EXAMPLE:

7.4 ml of 0.11 N Ceric Sulfate Titrating Solution were required to change the color of a 25 ml sample of water from red to light blue or blue green.

$$\text{Nitrite} = 7.4 \times 100 = 740 \text{ ppm NO}_2$$

NOTE: To express nitrite levels as ppm sodium nitrite ( $\text{NaNO}_2$ ) multiply ppm  $\text{NO}_2$  by 1.5. EXAMPLE: 740 ppm  $\text{NO}_2$  is equal to 1.5 X 740 or 1110 ppm as  $\text{NaNO}_2$ .

# TABLE B-14. CHLORIDE

## TEST PROCEDURES

### APPARATUS:

Burette, 10 ml Automatic (for Mercuric Nitrate Solution) (item 1001)  
 Bottle, w/Dropper (for Chloride Indicator Solution), 2 oz (item 1005)  
 Graduated Cylinder, 50 ml, Plastic, (item 1004)  
 Casserole, Porcelain, Heavy Duty, 200 ml Capacity (item 1003)  
 Stirring Rod, Plastic (item 1006)

### REAGENTS:

Standard Mercuric Nitrate Solution, 0.0141 N (item 2014)  
 Chloride Indicator Solution (item 2045)  
 Standard Sulfuric Acid Solution, N/50 (item 2001)

### METHOD:

1. Measure the amount of the water to be tested in the graduated cylinder. The amount should be based on the expected results of the test according to the following:

Chloride Expected, as Cl	Sample Size	Factor
Less than 20 ppm	100 ml	10
More than 20 ppm	50 ml	20

2. Pour into the casserole.

3. Add 10 ml of Chloride Indicator Solution to the water in the casserole and stir for 10 seconds. The color of the water should be a green-blue color at this point.

4. Add the Standard Sulfuric Acid Solution a drop at a time until the water turns from green-blue to yellow.

5. Squeeze the rubber bulb to force the Standard Mercuric Nitrate Solution from the bottle to fill the burette just above the zero mark; then allow the excess to drain automatically back into the bottle.

6. While stirring the water constantly, add Standard Mercuric Nitrate Solution slowly from the burette to the casserole until a definite purple color appears. This is the end point. (The solution will turn from green-blue to blue a few drops from the end point.) Read the burette to the nearest 0.1 ml.

RESULTS:

The chloride, in ppm Cl, is calculated as follows:

$$\text{Chloride, ppm Cl} = (\text{ml of Mercuric Nitrate} - 0.2) \times \text{Factor}$$

EXAMPLE:

11.2 ml of 0.0141 N Mercuric Nitrate Solution were required to change the color of a 50 ml sample of water from a green-blue to purple.

$$\text{Chloride} = (11.2 - 0.2) \times 20 = 220 \text{ ppm}$$

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